TECHNICAL METHODS OF CHEMICAL ANALYSIS

LUNGE AND KEANE'S

TECHNICAL METHODS

OF

CHEMICAL ANALYSIS

SECOND EDITION

EDITED BY

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PREFACE

THE sections in this volume of *Technical Methods of Chemical Analysis* have for the most part been completely rewritten for this edition, so as to include modern methods of analysis. The increase in the standardization of methods renders necessary a careful comparison of the procedures adopted, while in industries in which standardization has hardly yet begun a record of accepted practice is desirable.

The sections on the Gas Industry and on Tar and Tar Products have been augmented to include the detailed examination of the varied products now made. The short section on Calcium Carbide and Acetylene has been revised to accord with modern practice. The articles on Explosives, Matches and Fireworks (which have already appeared in a separate volume) have been brought up to date. The considerable portion of the volume devoted to Textiles and Textile Chemistry includes a wide range of material not hitherto brought together. The varied tests required for the investigation of textile materials and of the treatments to which they are subjected have been thoroughly dealt with.

It is obviously impossible to produce a volume of this sort without extensive conscious and unconscious utilization of material which has appeared in chemical literature. Particular acknowledgment is due to the Standardization of Tar Products Committee and to the British Standards Institution for permission to quote from their publications and to reproduce illustrations. The standard specifications of the British Standards Institution mentioned may be obtained from the office of the Institution (28 Victoria Street, London, S.W. 1) at a price of 2s. each plus postage, except where a different price is mentioned in the footnote in the text of this volume. The editor and authors also wish to acknowledge with gratitude the assistance of other organizations and friends too numerous to mention severally.

Many of the drawings for illustrations have been supplied by the authors of the various sections. It is desired, however, to record here the thanks of the editor and authors to the following organizations

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All data are calculated from the latest available figures, with such approximations as are usual in the technical work in which they are used. Temperatures are stated in degrees *Centigrade* unless other scales are specially indicated.

P. C. L. THORNE

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ABBREVIATED TITLES OF JOURNALS

Abbreviations.	Journals.
Amer. Chem. J.	American Chemical Journal
Amer. Petroleum Inst. Bull.	American Petroleum Institute Bulletin
Analyst	The Analyst
Angew. Chem.	Angewandte Chemie
Annalen	Annalen der Chemie
Ann. Physik	Annalen der Physik
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie
Annali Chim. Appl.	Annali di Chimica Applicata
Ann. Chim. Phys.	Annales de Chimie et de Physik
Ann. Mines Roumanie	Annales des Mines de Roumanie
Apoth.-Zeit.	Apotheker-Zeitung
Archiv. f. Hyg.	Archiv für Hygiene (und Bakteriologie)
Arch. Pharm.	Archiv der Pharmacie
A.S.T.M. Standards	American Society for Testing Materials, Standards
Beiblatter	Beiblatter zu den Annalen der Physik
Ber.	Berichte der deutschen chemischen Gesellschaft
Boll. chim. farm.	Bollettino chimico farmaceutico
B. P.	British Patent
B.S.	British Standard Specification
Bul. Soc. Romane Stiin.	Bulitenul Societatii Romane de Stiinte
Bull. soc. chim. Yougoslav.	Bulletin de la société chimique du royaume de Yougoslavie
Bull. Soc. Chim. Belg.	Bulletin de la Société chimique de Belgique
Bull. Soc. Chim.	Bulletin de la Société chimique de Paris
Chem. and Ind.	Chemistry and Industry
Chem. Fabrik	Chemische Fabrik
Chem. News	Chemical News
Chem. Ztg.	Chemiker Zeitung
Chem. Ind.	Chemische Industrie
Chem. Zentr.	Chemisches Zentralblatt
Chem. and Drug.	Chemist and Druggist
Chem. Weekblad	Chemisch Weekblad
Chim. et Ind.	Chemie et Industrie
Corps Gras Ind.	Corps Gras industriels
Comptes rend.	Comptes rendus hebdomadaires des séances de l'Académie des sciences
Dingl. polyt. J.	Dingler's polytechnisches Journal
Farben-Zeit.	Farben-Zeitung
Fuel	Fuel in Science and Practice
Gas J.	Gas Journal
Gas-. u. Wasserfach	Das Gas- und Wasserfach
Gazz. Chim. Ital.	Gazzetta Chimica Italiana
Ger. Pat.	German Patent
Ges. Abhandl. Kenntn. Kohle	Gesammelte Abhandlungen zur Kenntnis der Kohle
Gluckauf	Gluckauf: Berg- und Hüttenmannische Zeitung (Essen)
Helv. Chim. Acta	Helvetica Chimica Acta
Ind. Eng. Chem.	Industrial and Engineering Chemistry
Jahresber. f. Chem.	Jahresbericht für Chemie

ABBREVIATIONS.	JOURNALS.
J. Amer. Chem. Soc.	Journal of the American Chemical Society
J. Chem. Soc.	Journal of the Chemical Society
J. Franklin Inst.	Journal of the Franklin Institute
J. Gasbeleucht	Journal für Gasbeleuchtung und Wasserversorgung
J. Gas Lighting	Journal of Gas Lighting
J. Inst. Petroleum Tech.	Journal of the Institution of Petroleum Technologists
J. Pharm. Chim.	Journal de Pharmacie et de Chimie
J. Phys. Chem.	Journal of Physical Chemistry
J. prakt. Chem.	Journal für praktische Chemie
J. Soc. Arts	Journal of the Royal Society of Arts
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry
J. Soc. Dyers and Col.	Journal of the Society of Dyers and Colourists
J. usines gaz	Journal des usines à gaz
Kolloid Z.	Kolloid Zeitschrift
Kunstseide	Die Kunstseide
Mell. Textilber.	Melliand Textilberichte
Mém. poudres	Mémorial des poudres et salpetres
Mitt. Inst. Kohlenvergasung, Wien	Mitteilungen des Instituts für Kohlenvergasung und Nebenproduktgewinnung, Wien
Mitt. Materialprüf.	Mittheilungen aus dem Materialprüfungsamt zu Gross-Lichterfelde West
Monatsh.	Monatshefte für Chemie der kaiserlichen Akademie der Wissenschaften, Wien
Monatsbull. Schweiz. Ver. Gas- u. Wasserfachm.	Monatsbulletin Schweizerischer Verein von Gas- und Wasserfachmannern (Zürich)
Munic. Eng.	Municipal Engineering
Pharm. J.	Pharmaceutical Journal
Pharm. Weekblad	Pharmazeutisch Weeklbad
Pharm. Zeit.	Pharmazeutische Zeitung
Phys. Rev.	Physical Review
Pogg. Ann.	Poggendorf's Annalen der Physik
Proc. Phys. Soc.	Proceedings of the Physical Society of London
Rev. chim. ind.	La Revue de chimie industriel
Rev. Gén. Mat. Col.	Revue Générale des Matières Colorantes
Rev. gén. teint. blanch.	Revue générale de teinture, impression, blanchiment, apprêt (TIBA)
Rev. R. Acad. Cienc. Madrid	Revista de la Reale Academia de ciencias exactas, fisicas y naturales de Madrid
Rec. trav. chim.	Receuil des travaux chimiques des Pays-Bas et de la Belgique
Schweiz. Apoth.-Ztg.	Schweizerische Apotheker-Zeitung
Stahl. u. Eisen	Stahl und Eisen
Textilber.	Textilberichte über Wissenschaft, Industrie und Handel
Trans. Faraday Soc.	Transactions of the Faraday Society
Z. anal. Chem.	Zeitschrift der analytischen Chemie
Z. angew. Chem.	Zeitschrift für angewandte Chemie (continued as Angewandte Chemie)
Z. anorg. Chem.	Zeitschrift der anorganische Chemie
Z. Farb.- u. Text Ind.	Zeitschrift für Farben- und Textil-Industrie
Zentr. Gewerbehyg.	Zentralblatt für das Gewerbehygiene und Unfallverhütung
Z. ges. Schiess- u. Sprengstoffw.	Zeitschrift für das gesamte Schiess- und Sprengstoffwesen
Z. physikal Chem.	Zeitschrift für physikalische Chemie
Z. Verein. deutsch. Ingen.	Zeitschrift des Vereins deutscher Ingenieure

CONTENTS OF VOLUME IV

CALCIUM CARBIDE AND ACETYLENE

EXPLOSIVES

MATCHES AND FIREWORKS

COAL GAS

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In describing the various methods of analysis which are employed in the carbonizing industries, the normal sequence of manufacturing operations is followed as far as possible.

In the first place, consideration is given to the raw materials of the industry, *i.e.* coal, oil, refractory materials and iron oxide for the removal of hydrogen sulphide. The gas-making operations are then followed from the retorts through the purification processes to the finally purified gas as it is distributed for public consumption. Finally, consideration is given to the methods of analysis employed in the examination of the various products, *i.e.* coke, tar, ammoniacal liquor, etc.

I. RAW MATERIALS

A. Coal

The sampling and analysis of coal is of primary importance in the manufacture of coal gas. From the proximate analysis, some indication of the gas-making value of a coal may be obtained. Excessive moisture is undesirable as heat is required for its evaporation, and an increased volume of weak ammoniacal liquor is obtained. High ash content is equally undesirable as it seriously depreciates the value of the coke. From the volatile matter content a rough indication of the gas yield may be obtained.

(1) Sampling

The principles and methods employed in sampling coal are discussed in Vol. I., p. 327. Recently, standardized methods of sampling have been published by the British Standards Institution, to which reference should be made, as they are now largely adopted. Details of these methods will be found in the following publications :—

(1) Report on sampling small fuel up to three inches. E. S. Grumell and A. C. Dunningham. *B.S.* 403, 1930.

(2) British Specification for sampling. Analysis of coal for inland purposes. *B.S.* 420, 1931.

(3) Sampling of large and run of mine coal. *B.S.* 502, 1933.

(2) Analysis

Proximate Analysis. This comprises the estimation of moisture, ash, volatile matter and fixed carbon. Details of the various methods employed for the determination of these properties are given in Vol. I., p. 329 *et seq.* These tests have now been modified and standardized by the British Standards Institution (*loc. cit.*, No. 420, 1931). In regard to volatile matter there are three alternative methods, *i.e.* the crucible method, the muffle method in which the volatile matter is driven off at a definite temperature in a muffle furnace, and Lessing's method in which the coal is heated in a small silica retort. The volatile matter test is largely empirical, and hence it is essential that the carefully standardized procedure be followed, whichever method be adopted.

Coking Power. The coking power of a coal is next in importance to the gas-making value. The test is a measure of the maximum quantity of sand which can be mixed with a given weight of coal to give, on coking, a product which is strong enough to withstand the pressure equivalent to a 500 g. weight. The coke button which is formed in the test may support the above weight, despite the fact that a considerable proportion of the original mixture has not been cemented together. It is therefore necessary to limit the proportion of loose powder ; this is arbitrarily fixed at 5 per cent.

The sand used in the test must be composed of sharp-edged granules, rounded particles yielding lower results, and must be of such fineness that it will pass a No. 52 B.S.S. sieve, and remain on a No. 60 B.S.S. sieve. The requisite proportions of finely powdered coal and sand are weighed so as to give exactly 25 g. of mixture, and transferred to a tared, stoppered, cylindrical weighing bottle. They are then thoroughly mixed and transferred to a platinum crucible, the bottle being rotated continuously during the process to prevent the separation of the constituents of the mixture. The charged, covered crucible is placed on a platinum or nichrome wire triangle, and adjusted so that its base is 1 cm. above the top of a No. 4 Meker burner. The crucible is heated for seven minutes in the full flame of the burner and allowed to cool. A smooth cork is then placed on the surface of the coked mass, and on the top of this a tared, shallow porcelain dish, bottom up. The whole arrangement is inverted, the crucible removed carefully, and the coked mass placed on a level surface. It is then tested by lowering a 500 g. weight gently upon it. The powder remaining in the porcelain dish is weighed, and its weight should not exceed 1·25 g.

Ultimate Analysis. The ultimate analysis of coal, *i.e.* carbon, hydrogen, nitrogen and sulphur is carried out according to the methods given in Vol. I., p. 335 *et seq.* As an indication of the gas- and

coke-making properties of a coal, the ultimate analysis is of relatively little value, and the determination of the majority of the elements present is rarely carried out.

Sulphur. The sulphur content is often determined as it gives some indication of the quantity of sulphur compounds which may be present in the gas. Standardized conditions for carrying out the Eschka method are embodied in *British Standard Specification*, No. 404, 1930, p. 30. Sulphur may also be estimated in conjunction with the determination of the calorific value by washing out the bomb after combustion, and determining the sulphur in the washings. This method is also standardized in the above Specification.

Phosphorus. The presence of phosphorus is of particular importance in relation to the use of coke in the smelting of iron ores, etc. As a number of different methods are in use, these have been carefully examined by the British Standards Institution and the following is now proposed, and claimed to be the most accurate and simplest of the various methods examined.[1]

The ammonium molybdate reagent is prepared as follows :—100 g. of pure molybdic acid (containing not less than 85 per cent. MoO_3) is dissolved in a mixture of 80 ml. of concentrated ammonia solution and 400 ml. of distilled water. The resulting clear solution is poured slowly, and with constant agitation, into 1 litre of nitric acid solution (density = 1·205). 50 mg. of sodium ammonium phosphate, dissolved in a small volume of water, is added, and the whole heated to 65° with frequent agitation. The solution is finally filtered and cooled before use. In carrying out the determination, the coal or coke is first burnt and the ash collected. Such a weight of ash is taken as contains approximately 1 mg. of phosphorus. This is ground to a fine powder, transferred to a small platinum crucible and treated with 10 ml. of concentrated nitric acid and 5 ml. of hydrofluoric acid. The mixture is then carefully evaporated to dryness, a further 20 ml. of concentrated nitric acid added, and evaporation continued until approximately 7 ml. of the solution remains. The contents of the crucible are then washed into a 250 ml. beaker, diluted to 80 ml. with distilled water, and boiled for fifteen minutes. The solution is then filtered, concentrated to approximately 50 ml. and a slight excess of ammonia solution added. After being rendered just acid with concentrated nitric acid, the solution is heated to 75°, and 30 ml. of warm ammonium molybdate solution added slowly and with constant agitation. The solution is heated for a further period of

[1] Reprinted by permission from *British Standard Specification*, No. 735, 1937, "Analysis of Coal and Coke for Performance and Efficiency Tests on Industrial Plant," official copies of which can be obtained from the British Standards Institution, 28 Victoria Street, London, S.W. 1, price 3s. 6d.

thirty minutes at 50°, and then allowed to stand for several hours. It is then filtered and the precipitate washed thoroughly with 0·1 per cent. potassium nitrate solution, care being taken to keep the precipitate wetted throughout the washing. The filter paper is then transferred to a conical flask, covered with distilled water, and 15 ml. of *N*/10 sodium hydroxide solution added. It is then warmed to 35° to 40° and the flask agitated in order to disintegrate the filter paper completely. During this process the flask should be fitted with a freshly charged soda-lime guard tube to prevent the carbonation of the alkali present. When cool, the solution is titrated with *N*/10 nitric acid solution, using phenolphthalein as indicator. Then :—

g. phosphorus present in the weight of ash taken = (ml. *N*/10 NaOH employed) − (ml. *N*/10 HNO_3 required) × 0·000135.

Calorific Value.—The calorific value of a coal is of little use as a guide to its gas-yielding properties, but may be determined to enable a thermal balance of the process to be constructed. For accurate results the calorific value is generally determined in the bomb calorimeter. Details of the apparatus and procedure involved are given in Vol. I., p. 347. To ensure consistent and reproducible results, the details of the method require careful standardization and the method proposed by the British Standards Institution will be found in *B.S.* 420, 1931.

Carbonization Assay of Coal. As an indication of the gas-making and coking value of a coal the above tests are necessarily of limited value, and wherever possible a coal should be examined by an actual carbonization assay. Formerly it was the practice to carbonize about 2 lb. of coal in a small iron retort, the products being treated in small-scale washers, purifiers, etc. On large works a full-sized setting may be allocated for test purposes together with the necessary purification plant. To carry out large and semi-large scale tests of this type a considerable amount of time is involved and several methods are now available whereby an assay giving gas, tar, liquor and coke yields can be carried out on a few grams of coal in the laboratory, the whole test taking only a few hours for completion. In this country the most widely adopted of these is the Gray-King Assay. The apparatus comprises a small silica retort heated in an electric furnace. A charge of 20 g. of coal is used and the volatile products collected in suitable receivers. By modification of the temperature and rate of heating, etc., it is possible to obtain results which compare quite closely with those obtained in horizontal retorts. It is difficult in a laboratory test to reproduce the large gas yields which are obtained in practice from the cracking of the liquid and gaseous hydrocarbons. In the Gray-King apparatus, a length of 3 inches in the front part of the silica retort may be packed with crushed silica brick. This is heated

independently of the retort, and the degree of cracking of the vapours in passing through this zone can therefore be controlled. In this way gas yields can be obtained which closely approach those of actual practice. As regards continuous vertical retorts, however, no assay apparatus gives results comparable with those obtained under works conditions. For further details see *Fuel Research Technical Papers*, Nos. 7, 21 and 24.

Fusion Temperature of Coal Ash. A knowledge of the fusibility of the ash of different coals is of considerable value in relation to the use of coal and coke in gas producers, water-gas plant, in fact, in any appliance for the combustion of coal or coke. The method generally adopted is to make a small cone with the ash obtained from the coal and then to observe the temperature at which this cone commences to deform when heated in a furnace to progressively increasing temperatures. The temperature of fusion varies according to whether the atmosphere is oxidizing or reducing, and provision must therefore be made to heat the ash cone in a definite atmosphere. Details of an apparatus and experimental procedure have now been standardized by the British Standards Institution.[1]

B. Gas Oils

Evaluation of Oils for Carburetting.—Petroleum oils are almost exclusively used for carburetting water-gas, the fraction known as "gas oil" being employed. Such oils are composed of a mixture of saturated and unsaturated hydrocarbons, aromatics and naphthenes in varying proportions according to the field from which the crude oil is obtained. Until recently the only method of evaluation was by means of a laboratory cracking test. Suitable methods of analysis are, however, now available, and attempts have been made to correlate composition and carburetting value. Generally speaking, the saturated, and probably the unsaturated, hydrocarbons appear to be responsible for the greater part of the gas formation. Aromatic compounds and naphthenes are of much less value than the open chain compounds owing, presumably, to their greater stability at high temperatures, and their tendency to condense.

Analysis of Gas Oils.—The following methods of analysis are given by Griffith.[2]

1. *Distillation Curve* : 200 ml. of the oil is distilled from a 250 ml. Jena flask of a standard size, as made by Schott, at such a rate that the whole process takes forty-five to sixty minutes. The flask is protected from draughts by an asbestos shield. The volumes collected at suitable temperatures, or the temperatures at which different volumes

[1] *B.S.* 453, 1932. [2] *J. Soc. Chem. Ind.*, 1928, 47, 21

have distilled, are used to construct the distillation curve, and the process is continued until about 5 per cent. or less residue remains. The rate of boiling must be kept as uniform as possible and should not be allowed to slacken appreciably towards the end. The thermometer used should be calibrated against a standard. The temperature at which half the distillate has passed over is taken as the "mean boiling point."

2. *Unsaturated Hydrocarbons.* 50 ml. of the total distillate is shaken for fifteen minutes with 200 ml. of 80 per cent. sulphuric acid solution (sp. gr. 1·73) at room temperature. After the mixture has settled for two hours the acid layer is run off and the residual oil washed with water, then with about 20 ml. of 10 per cent. sodium hydroxide solution, and finally with water again. The oil, as free as possible from water, is drained into a 100 ml. Jena flask and distilled to the same end-point as that reached in stage 1, the difference in volume before and after this treatment being due to the removal of unsaturated compounds. Although the residue at this temperature may appear to be paraffinic, it must not be assumed that the distillation should be continued to a higher temperature, as such substances are frequently formed by the action of sulphuric acid on unsaturated compounds. This emphasises the great importance of the second distillation, as a reading of contraction on acid washing is quite misleading.

3. *Aromatic Hydrocarbons.* 20 ml. of the oil free from unsaturated hydrocarbons is shaken violently for fifteen minutes with 50 ml. of concentrated sulphuric acid (sp. gr. = 1·84). The oil which separates after standing for two hours is washed as described under "Unsaturated Hydrocarbons," and its volume is measured directly with careful draining of the separator or tap-funnel. The change in volume is due to the removal of aromatic compounds. The residual oil should be dried overnight with calcium chloride before proceeding to the determination of the naphthenes, but if care is taken the oil can be separated from the strong acid and used at once without washing. The saving in time is considerable, and the error introduced is very small.

Recently it has been shown that sulphuric acid containing 2 per cent. of silver sulphate is better for the removal of the lowest members of the aromatic series. This precaution is scarcely necessary, however, when examining high boiling mixtures such as gas oils.

4. *The Naphthenes.* 5 ml. of filtered dry oil (obtained after the removal of the aromatic hydrocarbons) and 5 ml. of dry aniline (redistilled and filtered after drying with potassium carbonate or sodium hydroxide) are heated, with stirring, in a test-tube immersed in a glycerine bath. As soon as the cloudy mixture becomes clear

and homogeneous, heating is stopped, and the liquid allowed to cool slowly with stirring. The temperature at which cloudiness reappears is recorded as the "aniline solution point." The thermometer employed should be graduated to 0·1° between 50° and 100° and must be immersed in the mixture. The amount of naphthenes present is calculated as follows :—

(*a*) The mean boiling point of the original distillate (stage 1) is found from the distillation curve, since it is the temperature at which half the distillate has passed over.

(*b*) The zero aniline solution point corresponding with any mean boiling point is found from the curve (Fig. 1). This gives the solution point if there are no naphthenes in the oil.

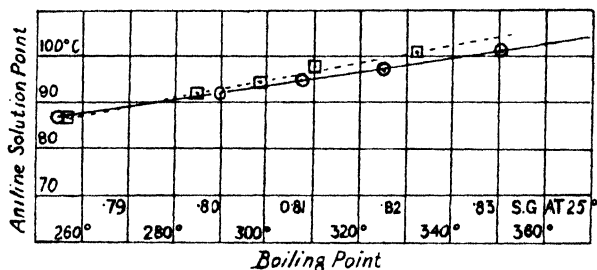



FIG. 1.

(*c*) The observed aniline solution point is subtracted from the zero point and for every 0·4° difference, 1 per cent. of naphthene is added ; thus if the zero point were 80° and that observed 76°, the depression of 4° would show that 10 per cent. of naphthenes were present in the paraffin-naphthene mixture.

In the following table are collected results given by Hollings [1] for the analysis of gas oils and the yield of gaseous therms on cracking. These figures show that the therms per gallon of oil are, in general, higher with the oils containing the greater proportion of saturated and unsaturated hydrocarbons.

Oil No.	Mean Boiling Point.	Paraffins. Per Cent.	Unsaturated Hydrocarbons. Per Cent.	Aromatics. Per Cent.	Naphthenes. Per Cent.	Maximum Therms per Gallon.
1	319°	81·7	0·0	0·0	18·3	1·45
2	277°	67·9	6·8	18·6	7·7	1·34
3	294°	60·4	9·7	16·7	13·2	1·30
4	299°	59·9	8·5	21·5	10·1	1·28
5	284°	61·0	6·6	10·7	21·7	1·31
6	288°	59·1	6·4	8·4	26·1	1·29
7	275°	52·3	7·2	22·3	18·2	1·19

[1] *The Manufacture of Gas*, vol. i., "Water-Gas." H. Hollings, London, 1934.

Cracking Tests on Gas Oils. The yield of gas obtained by cracking gas oil depends primarily on the temperature and, in addition, upon the nature of the carrying gas, its rate of flow, the rate of addition of the oil, the nature of the cracking surface, etc. Thus experimental results can be compared only with those obtained with an identical apparatus and when employing identical experimental conditions.

The apparatus used by Griffith [1] consists of an electrically heated silica tube 28 in. long. Oil from a water-jacketed burette passes through a small filter into a constant head tank which has a syphon overflow and a needle valve leading to the furnace. This tank is protected from warm air rising from the furnace by means of a shallow brass tank through which water is circulated, and the oil from it drops on to a number of steel balls carried on a grid inside the furnace. This is so placed that the oil is vaporized before it reaches the cracking zone and every precaution is taken to ensure complete control of the rate of oil feed. Hydrogen or other gases can be passed from a cylinder through a flow gauge to the furnace, and the gas and tar formed are cooled in a condenser. The cold gas is freed from tar fog in scrubbing tubes, metered, and burnt in a calorimeter. All tests are carried out under carefully standardized conditions. The following figures represent the results of a typical experiment [2] :—

B.Th.U. per cu. ft. mixed gas	904·5
B.Th.U. from oil	560·2
Therms per gallon of oil	1·205
Calorific value of oil gas	1868
Cu. ft. of gas/gallon of oil	64·0

A further apparatus and procedure has been standardized by the American Gas Association, and full details of this method are given in the *Gas Chemist's Handbook* (1922), published by this body.

Calorific Value. This figure is necessary for the calculation of the thermal efficiency, etc., of the water-gas process. The bomb method used for coal may be adopted except that in place of the coal 0·5 g. of oil is weighed into the platinum pan and the firing wire is arranged to pass through the oil.

Viscosity. This is useful as indicating the ease with which the oil can be handled at different temperatures. The Redwood viscometer may be used.

Sulphur Content. Oils of high sulphur content are undesirable since they increase the hydrogen sulphide in the resultant gas. The sulphur may conveniently be estimated in conjunction with the determination of calorific value as for coal, coke, etc.[3] A more convenient method is the sodium peroxide method : into a 100 ml. nickel crucible is weighed an intimate mixture of 17 g. of sodium peroxide and 0·5 g.

[1] *J. Soc. Chem. Ind.*, 1929, **48**, 252. [2] Hollings, *loc. cit.*, p. 83. [3] Vol. I., p. 335.

of potassium chlorate. Then 0·5 g. of the oil is added and mixed thoroughly with the fusion mixture by means of a glass rod. The crucible is covered and supported on a triangle placed on the rim of a 400 ml. beaker which has been filled with water. The crucible will thus be immersed to one-third of its depth in the water. The contents of the crucible are ignited by means of a fuse through a hole in the centre of the cover. This fuse is made by soaking cotton cord in a strong solution of potassium nitrate and drying. When the combustion is finished, the crucible is removed from the water, and the bottom struck gently so as to loosen the mass. The contents are washed with hot water into a 600 c.c. beaker, the solution boiled, acidified with hydrochloric acid and filtered. To the filtrate is added about 10 c.c. of bromine water, the excess bromine boiled off, and barium chloride solution added. The solution is then boiled for two hours, and if possible, should be allowed to stand overnight on a sand bath. The solution is then filtered, the precipitate washed with hot water, dried, ignited and weighed.

$$1 \text{ g. } BaSO_4 \equiv 0{\cdot}1374 \text{ g. Sulphur.}$$

C. Refractory Materials

The selection and use of suitable refractory materials for the construction of retort settings, producers, etc., is of the greatest importance to the gas engineer. The majority of the tests which are employed are complicated, and outside the scope of all except the largest undertakings who can provide a laboratory specifically for this purpose; otherwise the tests are carried out by the Research Associations and by the manufacturers of the various types of materials. The following tests are included in the Institution of Gas Engineers Specification [1] for refractory materials :—

1. **Chemical Analysis.**—No limiting figures for any constituents are included, a complete analysis being subject to agreement between

	Refractory Bricks.			Fireclay Retort Material.
	Fireclay Brick.	Siliceous Brick.	Silica Brick.	
SiO_2	69·76	89·00	95·52	78·55
TiO_2	...	0·70	...	...
Al_2O_3	25·56	8·60	1·06	18·53
Fe_2O_3	1·79	0·70	0·85	1·33
CaO	0·60	0·24	1·92	0·35
MgO	0·38	0·13	0·09	0·09
Alkalis	1·00	0·40	0·35	1·15
Loss on analysis	0·91	0·23	0·21	0·00
Total	100·00	100·00	100·00	100·00

[1] *Standard Specifications for Refractory Materials for Gas Works*, Institution of Gas Engineers, 1934.

the parties concerned. For details of the methods for carrying out a complete analysis of retort and other refractory materials, see Vol. III., p. 2 *et seq*. The preceding table (p. 9) represents typical analyses of refractory materials.

2. **Refractoriness.** The test-piece, cut from the body of the brick or block, and not including any of the original face, is ground in the dry state, on a suitable wheel, such as one of carborundum or emery, to the shape of a pyramid with a triangular base with one edge perpendicular to the base, and of the following dimensions :—

Sides of triangular base . . .	$\frac{3}{4}$ inch
Height of test-piece	$1\frac{1}{2}$ inches

A tolerance of $\frac{1}{16}$ in. may be allowed in these dimensions, but when the base is larger (within the tolerance) the height must be correspondingly larger (within the tolerance) than $1\frac{1}{2}$ in., and vice versa, since the shape and size of the test-piece are extremely important.

The test-piece is cemented on to a refractory disc with a refractory cement (consisting of calcinated alumina and 10 per cent. of the best china clay), with the perpendicular edge vertical. This last condition is very important. Five Seger cones, comprising the specified cone and those immediately above and below, are placed at regular intervals round the test-piece and equidistant from it. Care should be taken that the perpendicular edges of the cones are placed vertically.

The test-piece with the surrounding Seger cones is placed in a suitable furnace and the temperature raised at the rate of 50° per five minutes after about 1000° has been reached. The test must be carried out in an atmosphere containing free oxygen. When the specified cone has bent tip to base the test-piece is immediately removed from the hot zone and afterwards examined for signs of fusion. The signs adopted are either (1) the angular edges of the test-piece beginning to lose their angularity, or (2) the test-piece showing signs of bending, or (3) the matrix running out. The bending, if doubtful, can be judged by the use of a straight-edge on the original vertical edge.

If a gas-heated furnace is used, direct flame contact with the test-piece and cones must be avoided, and if an electric furnace is used, local " hot spots " must be avoided.

It is contemplated that the standard test should be made on only one test-piece at a time, when carried out in a vertical tube furnace. Should more than one test-piece be placed in the furnace for experimental purposes, care should be taken that the temperature is uniform over all the test-pieces.

The above test shows whether the material begins to soften at the specified cone and should not be confused with the well known test for refractoriness, which gives the squatting point of the material.

3. **After-Contraction or Expansion.**—Two test-pieces, 2½ in. to 3 in. in length and 1½ in. to 2 in. in width and in breadth—representative of the whole piece of material—are cut out. The opposite ends are ground parallel on a suitable wheel such as one of carborundum or emery and the length measured by means of a gauge to 0·002 in. or 0·005 cm. It is necessary to outline the position of the calipers at the initial measurement with a suitable refractory marking mixture, in order that the test-piece may be measured in the same position after firing. The test-pieces should be supported vertically in the furnace on some granular refractory material such as carborundum to prevent "sticking." A suitable gas-fired furnace, with blast if necessary, is used to fire the pieces. The test should be conducted in an atmosphere containing free oxygen.

To ensure the test-pieces being uniformly heated throughout and to avoid the formation of cracks in the case of silica material, at least four hours should be taken to attain the final soaking temperature. The furnace is maintained at this temperature for two hours. The average soaking temperature is 1450° for silica material and 1410° for siliceous material, firebricks, blocks tiles and retort materials ; the temperature during the early stages of the firing should be raised very slowly. Temperature readings should be taken every fifteen minutes, and it is essential that, when the final temperature has been reached, it shall be maintained practically constant—*i.e.* it shall not vary more than ± 20°. If it is necessary to remove plugs, etc., for the purpose of measuring temperature, great care must be taken to avoid cooling the furnace.

When the test-piece is cold, the length is again measured and the percentage alteration in size calculated. The average of the two results constitutes the "after-contraction or expansion."

When one test-piece is cut from an end and the other from the middle of a sample, some difference in the two results may be noted. It may be desirable then to report both results and not the average.

4. **Apparent Porosity.**—For methods of determining porosity, see Vol. III., p. 93 *et seq.*

5. **Cold Crushing Test.**—The machine required for the measurement of the crushing strength is so expensive that it will generally be necessary to have the tests carried out in a suitably equipped laboratory. The method to be employed is often to be determined by the capacity of the machine. The measurements on which the data stated in the specification were based were made in a large Avery machine with whole bricks placed with their long sides vertical between the jaws of the machine, giving a vertical thrust. The most important factors requiring attention are—

(1) The two ends of the brick which come into contact with the jaws of the machine must be ground flat and parallel on a suitable wheel, so as to receive a vertical thrust.
(2) An average of not less than three bricks must be used, because flaws, etc., may give an abnormal result, which might not be detected if only one brick were tested.

In addition to the tests embodied in the above specification, a number of other tests have also been developed. The refractoriness of a material as determined by the above test is not a criterion of its behaviour in practice, when it may be subjected to a considerable load which, generally, has the effect of reducing the refractoriness. It is therefore necessary to determine the refractoriness under load. A description of the apparatus employed for this purpose is given in Vol. III., p. 89 *et seq.*

Another interesting property is the thermal expansion of refractory materials. For this measurement the apparatus devised by Hodsman and Cobb may be used (see Vol. III., p. 80). This test does not attempt to measure the reversible expansion which may take place. For measurement of the reversible expansion over a range of temperature, Coppée's apparatus may be used (Vol. III., p. 127).

Specifications for Refractory Materials

The following specifications have been issued by the Institution of Gas Engineers [1] and other bodies for the following classes of material :—

A. Silica and Siliceous Bricks, Blocks and Tiles.
The material covered by this specification is divided into two classes :—
(1) That containing 92 per cent. and upwards of silica and hereinafter called " silica " material.
(2) That containing more than 78 per cent. but not more than 92 per cent. of silica, and hereinafter called " siliceous " material.

B. Fireclay Blocks, Tiles, etc. Containing not more than 78 per cent. silica.

C. Moulded fireclay and siliceous retorts. The moulded retort is defined as a complete section of retort without longitudinal joints, manufactured from any fireclay or siliceous material. (*N.B.* Retorts in segmental form shall come within the specifications for silica, siliceous, or fireclay bricks, blocks or tiles in Sections A and B.)

[1] *Standard Specifications for Refractory Materials for Gas Works*, Institution of Gas Engineers, 1934.

A. Silica and Siliceous Bricks, Blocks and Tiles.

Refractoriness Safety Test. Test-pieces of the material shall show no "signs of fusion" when prepared and heated in a suitable furnace, to :—

(1) not less than Seger cone 30 (about 1670°) for silica material.
(2) not less than Seger cone 29 (about 1650°) for siliceous material.

After-Contraction or Expansion. Silica Material. Test-pieces, when prepared, heated to 1450°, and maintained at that average temperature for two hours according to the method described, shall not show an after-contraction or expansion of more than 0·5 per cent., a tolerance of 0·1 being allowed for experimental error.

Siliceous Material. Test-pieces, when prepared, heated to 1410°, and maintained at this average temperature for two hours in accordance with the method described, shall not show an after-expansion or contraction of more than 0·5 per cent., a tolerance of 0·1 being allowed for experimental error.

B. Fireclay Blocks, Tiles, etc.

Refractoriness Safety Test. Two grades of material are covered by this specification, to be called respectively No. 1 and No. 2 Grades. Test-pieces of the material shall show no signs of fusion when prepared and heated in a suitable furnace to :—

(*a*) Not less than Seger cone 29 (about 1650°) for No. 1 Grade.
(*b*) Not less than Seger cone 26 (about 1580°) for No. 2 Grade.

N.B.—Firebricks which pass the refractoriness safety test at Cone 32 belong to the class of "Special Refractory Materials."

After-Contraction or Expansion. Test-pieces, when prepared, heated to 1410°, and maintained at this average temperature for two hours, shall not show an after-expansion or contraction of more than :—

(*a*) 0·75 per cent. for No. 1 Grade Material.
(*b*) 1·15 per cent. for No. 2 Grade Material.

A tolerance of 0·1 is allowed for experimental error.

C. Moulded Fireclay and Siliceous Retorts.

Refractoriness Safety Test. Test-pieces of material shall show "no signs of fusion" when prepared and heated in a suitable furnace to not less than Seger cone 28 (about1630°).

After-Contraction or Expansion. Test-pieces, when prepared, heated to 1410°, and maintained at this average temperature for two hours in accordance with the method described, shall not show an after-expansion or contraction of more than 0·75 per cent., a tolerance of 0·1 being allowed for experimental error.

D. Iron Oxide

It is customary to remove hydrogen sulphide from crude coal gas by passing the gas through oxide of iron, and details of the technique involved are discussed on p. 29. The iron oxide used for this purpose may be either natural or artificial oxide. The first type is found in naturally occurring deposits of oxide and organic matter and is generally known as bog ore. The majority of this material is obtained from Dutch and Belgian deposits, although small quantities of less active materials are found in this country. The artificial oxides are derived from a variety of sources. "Lux" is a by-product of the extraction of alumina from bauxite; other materials are based on the oxide residue left after removing the sulphur from spent oxide, etc.

In the following table are collected analyses of these various types of oxide.

Type of Oxide.	Moisture.	Organic Matter.	Insoluble Matter.	Ferric Oxide.	Activity of Ferric Oxide.
A. *Natural Oxides*—	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Belgian bog ore 1	10·75	19·92	19·39	41·42	48·80
Belgian bog ore 2	12·56	23·49	9·83	54·94	70·01
Dutch bog ore 1	22·22	8·11	7·55	44·27	35·80
Dutch bog ore 2	54·36	17·03	1·09	26·12	68·10
Dutch bog ore 3	44·70	18·53	6·13	30·54	37·00
B. *Artificial Oxides*—					
Metroxide	25·44	11·55	11·25	34·94	37·00
Lux	50·00	3·57	4·90	27·00	80·00
Regenerated Spent Oxide	33·99	15·45	6·06	32·94	45·00

Analysis of New Oxide

Sampling. The general principles of sampling are discussed fully in Vol. I., p. 4 *et seq.* The final bulk sample submitted for analysis is thoroughly mixed, and a number of 8 oz. samples drawn from it. One of these samples is taken for analysis, and if the material is extremely wet, it is advisable to weigh the whole 8 oz. sample accurately, and air dry for several hours. After reweighing, the material is ground in a mortar so that the whole of it passes through a No. 14 B.S.S. sieve. The analysis of the material can then be carried out, the results obtained being corrected back to the original moisture content. If the original oxide is sufficiently dry to handle and screen with ease, the preliminary air drying can be omitted.

Moisture. 10 to 20 g. of the sample is dried at 105° until a constant weight is obtained. The loss in weight represents the amount of moisture in the sample.

Loss on Ignition. 5 g. of the sample is weighed into a porcelain crucible, and heated over a Meker burner, cautiously at first, and

later with the full intensity of the flame. The loss in weight represents the amount of moisture and volatile matter.

Iron. The residue after ignition is transferred to a 300 ml. beaker and boiled for two hours with aqua regia. The solution is then diluted with water and filtered into a 500 ml. measuring flask, the filter paper being washed with hot distilled water until the filtrate obtained is colourless. When cool, the solution is made up to volume, an aliquot part taken, and the iron precipitated by the addition of a slight excess of ammonium hydroxide. The iron hydroxide is removed by filtration, washed with hot water, and redissolved in dilute sulphuric acid solution. After reduction with pure metallic zinc in the usual way, the final titration is carried out with *N*/10 potassium permanganate solution. The result is expressed as " total iron calculated as Fe_2O_3."

$$1 \text{ ml. } N/10\ KMnO_4 \equiv 0{\cdot}007985 \text{ g. } Fe_2O_3.$$

Alkalinity. 50 g. of the sample is treated with 250 ml. of distilled water, and allowed to stand for thirty minutes. The solution is then filtered and the filtrate titrated against *N*/10 sulphuric acid solution using methyl orange as indicator. The alkalinity is usually expressed as " percentage alkalinity calculated as Na_2CO_3."

Soluble Sulphates. 5 g. of the sample is boiled with 150 ml. of distilled water, the resulting solution filtered, and the filter paper washed free from sulphates with hot distilled water. The filtrate and washings are then acidified with concentrated hydrochloric acid, boiled, and the sulphate determined by precipitation with barium chloride solution in the usual manner.

Evaluation of Oxides of Iron for Removal of Hydrogen Sulphide

The value of an oxide of iron as a gas purifying material is dependent upon :—

(*a*) The proportion of iron oxide present.
(*b*) The reactivity of the oxide with hydrogen sulphide.

While the first factor is determined in the ordinary course of analysis, the second factor is considerably more difficult to assess. Two aspects must be considered, viz. :—

(*a*) The quantity of hydrogen sulphide which can be absorbed, irrespective of the rate of absorption.
(*b*) The rate of absorption.

The quantity of hydrogen sulphide absorbed can be determined by passing pure hydrogen sulphide through a tube packed with the oxide until there is no further reaction. The oxide is then removed and exposed to the air to convert the sulphide into the oxide, the revivified material then being recharged to the tube and again treated with

hydrogen sulphide. This operation may be repeated several times, and after each sulphiding a sample is taken and the sulphur content determined. The percentage of the total iron which reacts to form iron sulphide will be found to vary considerably, and this percentage is sometimes denoted by the term "active iron." Some comparative results for a number of oxides are given in the table on p. 14. While there is no agreed standard of procedure in carrying out this absorption test, it should be noted that the degree of fineness of the oxide, its moisture content, and the temperature of fouling, may appreciably affect the result obtained. Care should be taken that the oxide does not lose moisture prior to the test being carried out.

Various methods have been employed for the measurement of the rate of hydrogen sulphide absorption by an oxide. Possibly the most rational method is to pass coal gas containing about 1 per cent. of hydrogen sulphide (this being an average value in crude coal gas) through a layer of oxide at a constant rate. The rate should be arranged so that the velocity through the oxide is of the same order as in gas works practice, viz., about 1 to 3 ft. per minute. The volume of gas which is passed before any hydrogen sulphide appears at the outlet of the absorption vessel may be noted, and on continued passage of the gas the quantity of unabsorbed hydrogen sulphide may be measured from time to time. It is found that while two oxides will absorb equal quantities of sulphur when treated with pure hydrogen sulphide, one of these may allow unabsorbed hydrogen sulphide to pass almost immediately, while the other will continue to purify the gas for several hours. Alternatively, an oxide may allow hydrogen sulphide to pass after a relatively short time, but the quantity passing may then remain substantially constant.

It is essential that the oxide forms a fairly porous mass to allow the passage of the gas without undue resistance. Obviously, very finely divided material is unsatisfactory.

II. CARBONIZATION OF COAL

Control of the Carbonization Process

High temperature carbonization of coal for the manufacture of coal gas is operated so as to give the maximum yield of gaseous therms of any given calorific value. Under existing circumstances it is more economical to produce gas than tar, and carbonizing technique has been developed to this end. Carbonization at low temperatures (*i.e.* 600°) produces a high yield of tar and low yield of gas. As the temperature is increased, the gas yield rises due to additional gas being evolved from the semi-coke, and also by the thermal decomposi-

tion of the tar, yielding saturated and unsaturated hydrocarbons. The degree of cracking which is undergone by the tar depends upon the temperature and the time during which the tar vapours are exposed in the retort. When the latter factor is increased by only partly filling the retort with coal, the tar is excessively cracked and contains undue proportions of naphthalene and free carbon, while the additional gas obtained is negligible in quantity. In order that the maximum gas yield may be secured consistent with the maximum yield of tar of the required composition, it is necessary to examine periodically the composition of both the gas and the tar. The following figures [1] are indicative of the products obtained by carbonization in horizontal retorts under various conditions.

	1.	2.	3.	4.
Section of retorts (inches)	24×18	24×18	22×16	22×16
Charge of coal, lbs. per cu. ft. of retort space	28·5	35·2	38·4	28·6
Temperature of combustion chamber	1320°	1370°	1370°	1260°
Average time of carbonization in hours	13·6	13·6	10·1	13·0
Free carbon in tar, percentage dry basis	20·7	11·4	10·9	15·0
Inert-free gas—				
Calorific value B.Th.U./cu. ft.	628	620	614	653
Hydrogen. Per cent.	54·04	55·75	56·42	51·90
Methane. Per cent.	34·61	33·33	32·60	37·45
Carbon monoxide. Per cent.	7·75	7·35	7·48	6·80
Hydrocarbons (C_nH_m). Per cent.	3·59	3·57	3·50	3·85

The relative proportions of saturated and unsaturated hydrocarbons are indicative of the temperature and degree of carbonization, and the extent to which cracking of the products has taken place. The control of the carbonization process is thus dependent upon the analysis of the crude gas and tar. Methods of complete gas analysis are discussed on p. 43, while complete analysis of the crude tar is unnecessary and it is sufficient to determine the free carbon and tar acid content. In addition, the naphthalene content may be a useful guide to the degree of cracking which has been undergone by the tar. For methods of tar analysis, see p. 153 *et seq.* Generally speaking, low temperatures result in increased saturated and unsaturated hydrocarbons in the gas, and low free carbon and naphthalene, but higher tar acids, in the tar. Excessive temperatures are indicated by higher hydrogen content and low hydrocarbons in the gas, and higher free carbon and naphthalene in the tar.

[1] H. Hollings, *Gas J.*, 1928, **182**, 924.

A. Heating of Retorts

1. **Manufacture of Producer Gas.**—High temperature carbonization may be carried out in horizontal, intermittent or continuous vertical retorts, or in chamber or coke ovens. To maintain the retort or oven at the required temperature, producer gas or coal gas is burnt in suitable flues surrounding the retort. Whereas coke ovens are frequently heated by the gas evolved from the ovens themselves, it is almost universal practice to heat retorts which are employed for town's gas manufacture, by producer gas. This is manufactured by the passage of air and steam through heated coke. The air is drawn through the fuel bed by natural chimney draught, except where the gases leaving the setting pass through waste heat boilers, when the extra resistance necessitates the inclusion of a fan. The most common practice is to build the producer together with the brickwork of the retort setting, but in some cases separate producers are used. In the latter case the gas can be cooled and washed to remove the dust before combustion in the setting. To prevent unduly high temperatures at the base of the producer, it is the practice to allow a little water to flow over the bars, or better, to add some steam to the air supply. The water vapour or steam reacts with the coke, forming water-gas, the heat absorbed by this reaction being sufficient to maintain the required temperature at the base of the producer. In addition, this water-gas increases the heating value of the producer gas. The quantity of steam required depends upon the rate of gasification of the coke per unit of grate area. At low rates, the loss of heat through the walls of the producer and as sensible heat in the producer gas, is sufficient to maintain the temperature low enough to prevent fusion of the ash and the destruction of the producer bars and plates. At higher gasification rates the temperature increases progressively, and steam is required as a controlling medium. Excessive steam must be avoided since it reduces the temperature to a point at which the producer and water-gas reactions tend to produce carbon dioxide in preference to carbon monoxide. Further, it may result in the highest temperature zone being above the point at which the ash and clinker can be removed through the cleaning doors, the producer ultimately becoming completely blocked with clinker. The clinker and ash must be periodically removed, as their accumulation increases the resistance to the flow of air, and so reduces the volume of gas made.

2. **Control of Producer Operation.**—For efficient working it is necessary to measure and control the steam and water supply, and the draught from the main flue of the setting, as the volume of air drawn through the fuel bed depends on the latter. The steam supply is measured by any convenient form of steam meter, or more simply

by inserting an orifice in the steam line and calculating the rate of flow from the differential pressure across the orifice.

The draught at the base of the producer is usually of the order of 10 to 15 hundredths of an inch, while above the fuel bed there is often slight pressure. It is therefore necessary to use a gauge with a magnified scale. Many of these are now available, some being described in Vol. I., p. 167 *et seq.* A convenient inclined gauge for retort house use is manufactured by the Hayes Gauge Co. It is, however, more general practice to control only the draught in the main flue of the retort bench, this being applicable to all producers supplying the particular bench of retorts. In this case it is convenient to install a recording vacuum gauge, many types of which are now available. An instrument which is suitable for this purpose is the ring balance manometer.

The following diagram (Fig. 2) illustrates the principle of this apparatus. The glass or metal ring, pivoted at its centre, contains

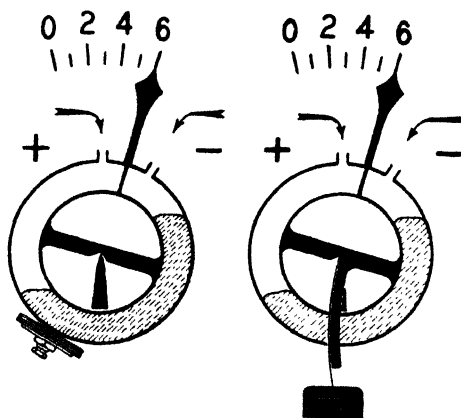



FIG. 2. FIG. 3.

a suitable sealing liquid. Any difference in the pressure exerted on the two liquid surfaces causes a proportional movement of the ring about its centre until equilibrium is again established. The pressure is transmitted to the liquid in the tube by flexible rubber connections. These instruments can be used for measurement of volume according to the differential pressures across an orifice.

In the "Union" ring balance apparatus (Fig. 3), a weight is suspended on a steel band in the centre of the ring balance which also carries a curved arm. In the zero position of the instrument the weight exerts no turning movement, as it is situated vertically below the centre of gravity. When the balance turns, the weight is deflected to the side by the curved arm so that it is no longer vertically

below the centre. The weight now exerts a turning movement opposing the deflection of the balance; the curvature of the arm is such that the turning movement caused by the weight causes the deflection to be proportional to the square root of the differential pressure.

3. Analysis of Producer Gas. The following table gives typical producer gas analyses as obtained with different types of producers and rates of gasification.

		External Producer. Mechanical Grate.	Internal Producer. Hand Clinkered.	External Producer. Non-mechanical.
Rate of Gasification. Lbs. of coke per sq. ft. grate area per hour		40-55	15	35-40
Per cent. composition of producer gas	CO_2	3·3	5·0	2·6
	CO	30·7	27·0	31·2
	CH_4	1·0	1·0	0·8
	H_2	9·0	6·0	10·0
	N_2	56·0	61·0	55·4
Calorific value: B.Th.U./cu. ft.		136·5	105·0	131·6

The proportions of carbon dioxide and monoxide are determined primarily by the temperature of the fuel bed, while the hydrogen content is dependent on the quantity of steam used.

The presence of methane is generally attributable to incomplete carbonization of the coke.

The sample of gas may be drawn from any convenient point above the fuel bed. A silica tube should be used for this purpose, together with a pair of sampling bottles (see Vol. I., p. 232 *et seq.*). For retort house control, only the carbon dioxide and carbon monoxide are usually estimated, the Orsat or similar apparatus being used (Vol. I., p. 272 *et seq.*). Periodical determination of the hydrogen content is, however, advisable; also the nitrogen content, as a check on the determination of the absorbable constituents. The hydrogen may be estimated by explosion or combustion in the Orsat apparatus, or for greater accuracy, in the Bone and Wheeler apparatus (Vol. I., p. 285). For the rapid determination of nitrogen, the Metrogas apparatus is suitable (Vol. I., p. 295). The following example illustrates the examination of these analyses :—

Producer Gas.	Per cent.
CO_2	5·0
CO	27·0
H_2	6·0
N_2	62·0 (by difference)
N_2	61·0 (by Metrogas apparatus)

To check the accuracy of the analysis, it is advisable to calculate the oxygen : nitrogen ratio, thus :—

	Per cent.
Oxygen equivalent of carbon dioxide	5·0
,, ,, carbon monoxide	13·5
	18·5
Less oxygen derived from the water decomposed . . .	3·0
	15·5
Equivalent nitrogen	58·59

In this example there is insufficient carbon dioxide and carbon monoxide to satisfy the oxygen equivalent of the nitrogen, probably owing to incomplete combustion.

It must not be assumed that a good producer gas analysis ensures adequate heating of the retorts. There must obviously be an adequate *volume* of gas, and after ensuring that the composition is as required, it is necessary to examine the draught and the quantity of clinker in the fuel bed in cases where there appears to be insufficient heat.

4. **Temperature Control in Carbonization.**—The carbonization of coal to give the maximum yield of products of the desired characteristics is dependent primarily upon the maintenance of the required temperature in the retorts. The throughput of coal per day for each retort is a function of this temperature, and for any size of retort there is a fixed temperature for a given throughput of coal. Departure from this temperature results in incomplete carbonization if the temperature be too low, or if too high the volatile products may be overheated. This may reduce the yield of tar and increase its free carbon content—an undesirable feature—while the gas will contain more hydrogen and a lower proportion of hydrocarbons. Hence temperature measurement and control is of primary importance. In the case of the horizontal retort, it is customary to control the temperature of the retorts by the temperature of the combustion chamber. The relationship between this temperature and that of the retorts themselves depends upon the design of the setting, and it is sometimes advisable to measure also the retort temperature and that of the flues where the gases leave the setting. In the case of vertical retorts, the heating gases pass round the retort in a series of flues, and it is customary to measure the temperature at different points in these flues. The settings can be worked to give high temperatures at the bottom or at the top of the retorts, and the difference in temperature between these points is varied according to the nature of the coal which is being carbonized. For temperatures of 900° or over, it is customary

to use some form of optical pyrometer. The Cambridge instrument (see Vol. I., p. 164) gives accurate and easily reproducible results. Another type is the Holborn-Kurlbaum disappearing filament optical pyrometer, which is described in Vol. I., p. 163. This principle is now embodied in the Foster Optical Pyrometer. In the latest modification of this instrument, known as the "Lamp-Bridge Unit," the lamp filament comprises one of the arms of a Wheatstone Bridge (see Fig. 4). The bridge is balanced at a definite temperature, *i.e.* 800°, and when the current to the lamp is increased for higher temperatures the bridge becomes unbalanced, the millimetre pointer moving correspondingly. The lamp and other resistances, A, C and

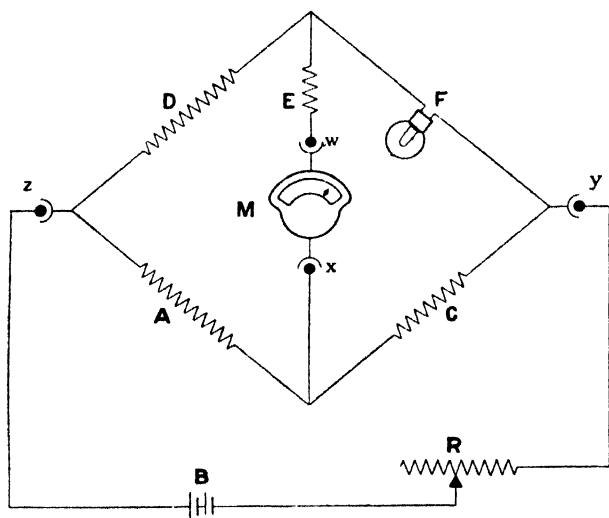
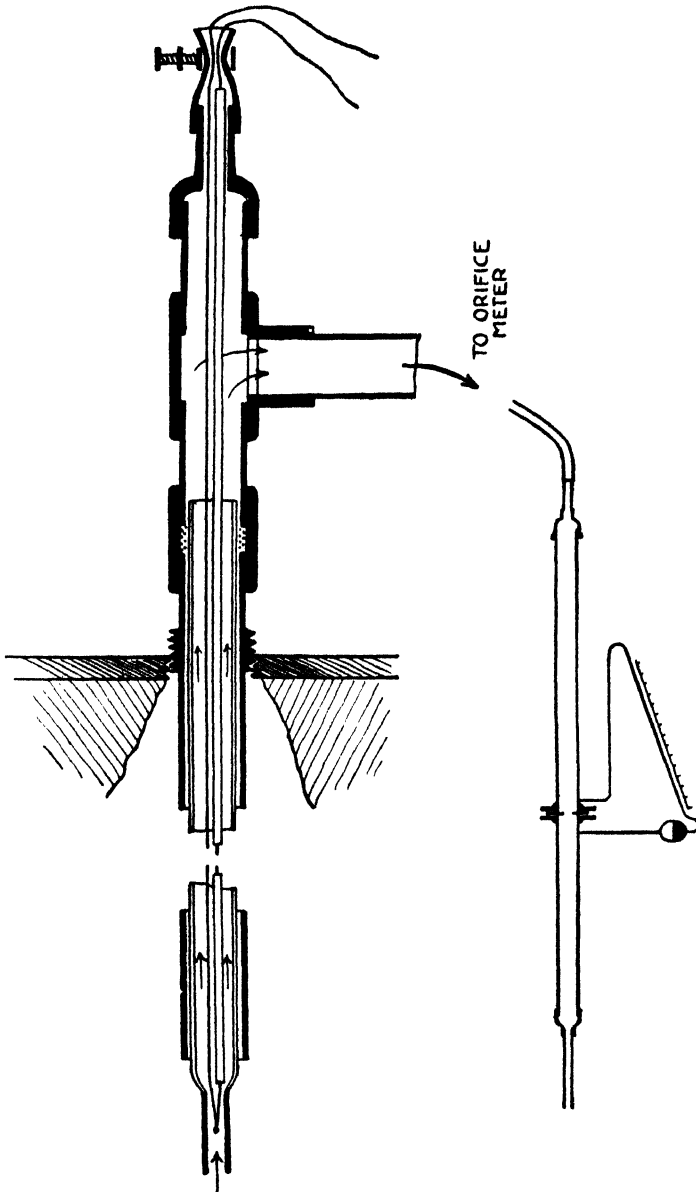



FIG. 4.

D in the circuit may be changed at will and the range of the instrument altered as required. For temperatures above 800° a mono-chromatic red glass is fitted over the eye-piece which simplifies the comparison of the filament and hot body illumination. For the measurement of the temperature of waste gas, secondary air, etc., a thermocouple is generally used as the temperature is too low for accurate registration with an optical pyrometer. If the wall temperature of a flue is above or below that of the flowing gas, some modification of the usual procedure is necessary. Thus, if the walls of the flue are at a higher temperature than the gas, the thermocouple will receive radiant heat from the walls and register a higher temperature than that of the gas. To overcome this difficulty, the thermocouple must be screened from radiant heat. A convenient method is to fit the couple inside an outer sheath through which is drawn a rapid stream of the gas.

The outer sheath cuts off the radiant heat and, provided the gas flow is sufficient, the true gas temperature is recorded. A suitable arrangement is given by Dent and is shown in Fig. 5.

Fig. 5.

The hot gas is pulled by means of a fan or other suitable apparatus through the outer tube ($\frac{5}{8}$ in. internal diameter) which surrounds the thermocouple and protects the latter from direct radiation from the walls of the flue. It is necessary to draw sufficient gas through the

tube to enable the couple to attain the true gas temperature. The rate of flow is therefore increased until there is no further increase in the temperature. It is usually found that the gas velocity through the tube should be 300 ft. per sec. to attain a correct temperature. For further details of this apparatus, see 32nd Report, Joint Committee of the Institution of Gas Engineers, 1932.

5. **Sampling and Analysis of Waste Gases.**—To ensure that the heating is being carried out efficiently the waste gases should contain a minimum of excess air. Generally an average of about 1 per cent. of oxygen is allowed ; if too fine a limit is set, excess carbon monoxide will, at times, be present. Immediately after cleaning the grate the volume of producer gas is at a maximum, and as the secondary air supply is constant the excess oxygen will be then at a minimum. As the resistance of the fuel bed increases owing to the formation of clinker, the producer gas output decreases and results in a greater proportion of excess oxygen. The variations in composition which are thus encountered are dependent upon the frequency of clinkering and the rate of gasification of the coke.

In order to avoid loss of carbon monoxide, gas samples should be taken when the excess air is at a minimum, *i.e.* immediately after clinkering. The gas should be drawn from the flue through a silica tube, using a convenient sampling apparatus (see Vol. I., p. 232). Samples should be taken before the regenerators since there is generally leakage of air into the waste gases ; samples taken before and after the regenerators are useful to determine the extent of such leakage. The waste gases are usually analysed in the Orsat or some modification of this apparatus (Vol. I., p. 272). It should be remembered that where hydrogen is present, the oxygen and carbon dioxide may not total to 20 per cent. The composition of the waste gases should be calculated for an average producer gas composition in order that the accuracy of the analysis may be checked by comparing the total carbon dioxide and oxygen with the nitrogen. The absence of oxygen and presence of carbon monoxide indicate insufficient secondary air and must be rectified by increasing the openings of the secondary air ports. In general, it is preferable to adjust the air in this way rather than to alter the main dampers, which will also increase the volume of producer gas. Some time should be allowed after any alteration so that conditions may become stable, as alterations in temperature will affect the draught and the volume of both producer gas and secondary air.

6. **Adjustment of Temperature in the Settings.**—Different retort temperatures are necessary in the setting according to the type of coal and the period of carbonization. The temperature is altered by increasing the volume of primary air to the producer and secondary

air to the combustion chamber. Experience indicates the port area required for the maintenance of any required temperature. Several hours are required for the setting to regain equilibrium after any such alteration. In the case of horizontal retorts, it is the practice to maintain the draught on the setting so that there is a zero or slight pressure in the combustion chamber. This is advantageous in that it prevents entrainment of cold air through the brickwork, and through any sight boxes, etc., which may exist. Otherwise the temperature may be lower at the ends of the retorts than in the centres, due to the loss of heat through the end-walls and retort mouth-pieces.

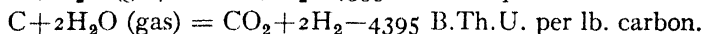
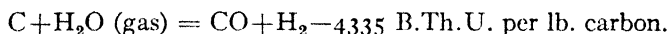
B. WATER-GAS

The manufacture of water-gas may be considered under two headings, viz. :—

(1) Blue Water-Gas ; *i.e.* water-gas as made by the passage of steam through heated coke.

(2) Carburetted Water-Gas ; gas oil is sprayed into a chequer-work carburettor, through which the blue water-gas is passed, the resulting oil-gas going forward with the blue water-gas to yield a mixture of higher calorific value.

1. **Blue Water-Gas.**—The manufacture of water-gas is dependent upon the following reactions :—

$$C+H_2O\ (gas) = CO+H_2-4335\ \text{B.Th.U. per lb. carbon.}$$
$$C+2H_2O\ (gas) = CO_2+2H_2-4395\ \text{B.Th.U. per lb. carbon.}$$

The data given above refer to the reactions at 15·5°. The second reaction, which is undesirable owing to the production of inert carbon dioxide, predominates at temperatures below 800°, and the first above this temperature. Both reactions are endothermic and air must be blown periodically through the fuel bed to generate the heat necessary to maintain the required temperature. The temperature falls continuously throughout the steaming or run period.

For the control of the process, temperature measurement is essential. Gas temperatures are generally measured at the outlet of the generator, carburettor and superheater and also before and after the waste heat boiler, where one is provided to reduce the temperature of the blow gases leaving the superheater. Temperatures are generally measured by means of thermocouples. When these are fitted with metal protecting sheaths—the general practice—there is a considerable lag. As the temperature of the hot gases is changing rapidly, the use of the sheathed thermocouple may thus yield erroneous results. For

works control the temperatures obtained in this way are sufficiently accurate, but for investigation purposes the hot junction of the couple should be in direct contact with the gases. To avoid radiation errors a screened pyrometer should be used (see p. 22).

Measurement of Gas Flow. Measurement of the volumes of air to blast and of water-gas is made difficult by reason of the rapid variations in rate of flow. Using an orifice or venturi meter, a continuous record can be obtained, the integration of which will give the required volume of gas. An investigation of this problem has been made by the Fuel Research Board (Technical Paper No. 27) who photograph the deflections of an inclined gauge caused by varying differential pressures across an orifice in the air or gas main.

Steam Measurement. The steam supplied to the generator can be accurately measured by the use of one of the various types of steam meters now available. Many of these are based upon the differential pressure caused by the flow of steam through an orifice of known diameter. In the absence of a meter, the quantity of steam may be calculated from the observed drop in pressure across the orifice in the steam main. Details of formulæ for the calculation of steam flow, etc., are given in *Technical Data on Fuel,* ed. H. M. Spiers, 1935.

Sampling and Analysis of Gases. It is difficult to obtain a representative sample of gas from the rapidly fluctuating flow in a water-gas plant. The composition of the blow and run gases changes continuously during each cycle and also between one charging period and another. The most satisfactory method is to take a series of " spot " samples and combine them into an average sample. Samples should always be taken over mercury. A convenient apparatus for combining such " spot " samples is discussed by Hollings [1] and shown in Fig. 6.

Measurement of Undecomposed Steam. This is conveniently made by drawing a sample of the gas through a series of calcium chloride tubes, any tar or dust being removed by a small cotton-wool filter.

Dust in Gas. During the blow period, fine particles of coke and ash are carried through the plant and escape from the stack. It is hence customary to fit some form of dust arrestor, and to ascertain the efficiency of this apparatus the dust content before and after may be determined. Details of the test for the determination of dust are given in the 31st Report of the Research Committee of the Institution of Gas Engineers, 1932.

Thermal Efficiency and Plant Balances. The compilation of weight and chemical balances of water-gas plants is complicated by the difficulty of accurately measuring the volume of blow gases. It

[1] *The Manufacture of Gas*, vol. i., "Water-Gas." H. Hollings, London, 1934.

is customary, therefore, to draw up a carbon balance from which the volume of blow gas can be calculated. Having obtained the volume of air supplied and the composition and volume of the resulting gases, it is possible to compile a thermal balance from which useful information concerning the effective utilisation of the thermal value of the coke (and oil) may be obtained. For details of the data and calculations involved, reference may be made to *The Manufacture of Gas*: "Water-Gas" (Hollings); Fuel Research Board Technical Report, No. 30;

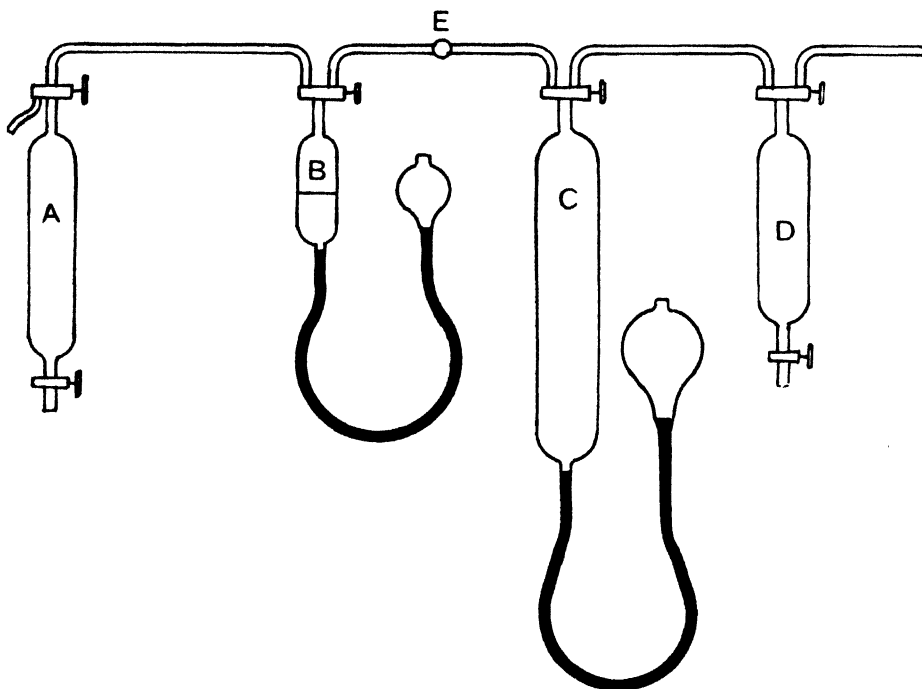



FIG. 6.—CUMULATIVE SAMPLING FOR ANALYSIS.

A. Snap Sample. B. Constant Volume Vessel. C. Reservoir for Accumulated Sample. D. Bulb for Analysis. E. Branch for Duplication of C and D.

6th and 7th Report of the Research Committee of the Institution of Gas Engineers, 1921 and 1922.

2. **Examination of Blue and Carburetted Water-Gas.**—Typical analyses of purified water-gas are given in the table on the next page.

The crude gas leaving the plant contains hydrogen sulphide, naphthalene, hydrocyanic acid, tar vapours, etc. These impurities may be estimated by the methods discussed under coal gas (see p. 28 *et seq.*). The crude gas is passed through condensers, tar extractors, and finally through oxide purifiers to remove the hydrogen sulphide. For the analysis of the purified gas, the methods given on p. 43 in reference to coal gas should be used.

Analysis of Carburetted and Blue Water-Gas at Various Stages in the Cycle (Hollings)

Typical Analysis of Water-Gas.			Variations in Composition of Gas during Run Period.					
			Blue.			Carburetted.		
	Blue Water-Gas.	Carburetted Water-Gas.	½ min.	2½ mins.	4½ mins.	½ min.	2½ mins.	4½ mins.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
CO_2	5·9	5·9	2·7	5·5	12·7	2·7	5·5	12·7
O_2	...	0·4	...	...	...	...	...	...
C_nH_m	...	7·0	...	...	...	7·9	8·2	0·7
CO	32·2	32·2	38·7	30·8	26·8	38·7	30·8	26·8
H_2	42·0	37·8	41·4	41·8	52·2	36·7	41·3	54·0
CH_4	0·5	9·1	...	...	...	6·7	8·8	−0·9
C_2H_6	...	2·2	...	...	...	2·7	2·5	1·3
N_2	3·8	5·4	...	...	...	4·6	2·9	5·4
H_2O	...	...	4·2	23·1	52·5	0·2	1·1	2·5

III. PURIFICATION OF CRUDE COAL GAS

Crude gas contains the following impurities which must be removed :—

1. Tar.
2. Ammonia.
3. Hydrogen sulphide.
4. Hydrocyanic acid.
5. Naphthalene.
6. Organic sulphur compounds.

In addition, benzole and water vapour may be removed.

The methods of sampling which should be used in the estimation of the above impurities in crude gas are discussed in Vol. I., p. 230.

1. **Tar.**—The majority of the tar is precipitated in the hydraulic and foul mains, the remainder being removed in the condensers and by the various types of tar extracting appliances. Of these the Livesey washer and the Pelouze and Adouin extractor are widely used, while more recently, tar removal by electrostatic precipitation has been introduced. This latter method is by far the most efficient, and reduces the tar content to a negligible value. For the control of this extraction plant it is necessary to determine the tar content of the crude gas. Two methods of determination are given in Vol. I., p. 318. Both these methods depend essentially on the filtration of the tar fog from the gas by suitable means.

A simple and ready method is to pass a measured volume of gas

through a coarse filter paper, the depth of the stain which is produced giving a measure of the quantity of tar fog present, or alternatively the paper may be weighed before and after the test. It should be appreciated that tar, as discussed above, refers to liquid particles entrained in the gas, and must not be confused with light oils actually present in the vapour phase. These latter can, obviously, only be separated after they have been condensed by cooling.

2. **Ammonia.**—After the removal of tar, the ammonia is extracted by washing the gas with a dilute solution of ammonia (gas liquor) and subsequently with water—the gas and liquid flowing in counter current. The ammonia should be reduced to some 2 to 3 grains/100 cu. ft. The ammonia content before and after the extraction plant is usually determined by passing a sample of the gas through standard acid and titrating the residual acid. For details see Vol. I., p. 312.

3. **Hydrogen Sulphide.**—This impurity is removed subsequently to the ammonia, usually by passing the gas through purifier boxes containing oxide of iron. The gas from horizontal and vertical retorts contains 400 to 700 grains/100 cu. ft. depending upon the type of coal carbonized. Water-gas contains a lower quantity, viz., 200 to 300 grains/100 cu. ft. Further details concerning the removal of hydrogen sulphide are given on p. 39.

General methods for the determination of hydrogen sulphide in gases are discussed in Vol. I., p. 303 *et seq.* In addition, the methods given below have been found satisfactory for gas works purposes.

When it is required to determine exactly the hydrogen sulphide content of the gas over a definite period, the following method may be adopted :—

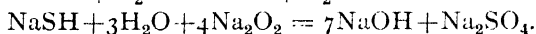
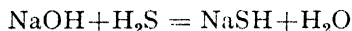
A solution of cadmium chloride is prepared by dissolving 160 g. of cadmium chloride in a litre of distilled water slightly acidified with hydrochloric acid. Three wash bottles are employed for the absorption of hydrogen sulphide, containing in the aggregate 250 ml. of the cadmium chloride solution. The gas, which is passed through the absorption bottles at a rate not exceeding 0·4 cu. ft. per hour for twenty-four hours, is measured at the outlet of the bottles by means of a meter.

When the absorption is completed, the bottles are disconnected and the cadmium sulphide filtered off. The contents of the filter, after careful washing, are placed in a beaker containing distilled water and oxidised to cadmium sulphate by means of bromine. The excess of bromine is removed by boiling and, if necessary, the resulting solution is filtered to remove impurities, the residue being carefully washed. The sulphate content of the filtrate is then determined in the ordinary way, after acidification with hydrochloric acid, by precipitation with barium chloride solution.

The hydrogen sulphide content is expressed as grains of hydrogen sulphide per 100 cu. ft. of gas corrected for temperature, pressure, and hydrogen sulphide content.

1 g. $BaSO_4 \equiv 2 \cdot 253$ grains hydrogen sulphide.

Approximate Methods for Works Purposes. The following method is suitable when it is sufficient to know the hydrogen sulphide content of the gas to within 1 grain per 100 cu. ft. It is based on the following reactions :—

$$NaOH + H_2S = NaSH + H_2O$$
$$NaSH + 3H_2O + 4Na_2O_2 = 7NaOH + Na_2SO_4.$$

Three wash bottles are employed for the absorption and contain respectively about 100 ml., 60 ml. and 40 ml. of 10 per cent. sodium hydroxide solution. The inlet of the wash bottles is connected to the main by a minimum length of glass tubing, whilst the outlet is fitted to a meter with a governor so set as to allow the passage of approximately 8 to 10 cu. ft. of gas in twenty-four hours. At the completion of the test period, the contents of the bottles are washed out and made up to a known volume. Of this solution, an aliquot part is taken and oxidised with sodium peroxide or bromine in the cold. The solution is then heated to boiling, acidified with hydrochloric acid, and its sulphate content determined by precipitation with barium chloride solution in the usual manner. The sodium hydroxide and sodium peroxide used in this test must be free from sulphate.

For the very rapid estimation of hydrogen sulphide for works control purposes, the method of Somerville (Vol. I., p. 305) has been found satisfactory.

Detection of Traces of Hydrogen Sulphide. For general information on this subject, see Vol. I., pp. 305-6. The use of lead acetate paper discussed in the above reference forms the basis of the Standard Gas Referees Test for hydrogen sulphide. This test is based on the assumption that one part of hydrogen sulphide per million will produce a visible stain on a lead acetate paper in three minutes. While the test is really qualitative, it is possible to estimate the quantity of hydrogen sulphide from the depth of the stain produced. Full details of the test are given in " The General Notification of the Gas Referees, 1934."

Determination of Traces of Hydrogen Sulphide. The question of the quantitative determination of hydrogen sulphide in coal gas has been investigated recently by Hollings,[1] who proposes a method involving the determination of the optical density of a lead sulphide stain. If the fullest precautions are taken it is claimed that very accurate results can be obtained.

[1] Hollings and Hutchison, *Chem. Ind.*, 1935, 726, 752.

In carrying out the test, the gas under analysis should be brought to the apparatus by the shortest possible route, glass tubing being used for the connections. The gas should be saturated with water at the temperature of testing.

The apparatus used is illustrated in Fig. 7. The gas enters through regulating tap A and the tube B, which contains a small piece of damp pleated filter paper. The flanges C, C_1 have their faces ground true on a plane surface, and the apertures are ground internally to exactly ½ in. diameter. They are held firmly together, with a piece of test paper between them, by means of brass clips or other suitable device to obtain a strong pressure. A calibrated flow gauge, or a test meter, can be used for the gas measurement, but the apparatus should not be subjected to undue pressure. Gas is passed at approximately 1 cu. ft. per hour for a specified period, and

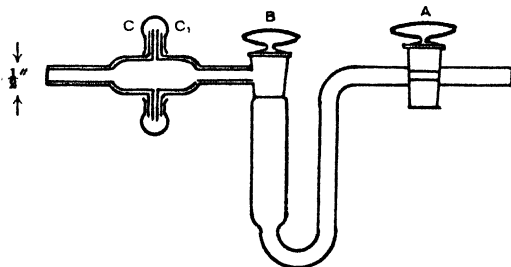



Fig. 7.

at the end of the test no coloration should be visible on the back of the test paper. The measure of the depth of the stain on the test paper depends on the proportion of the incident light that it will transmit. Thus a density of value x is such that it will transmit 10^{-x} of the incident light. A convenient method of measuring the density is provided in the Sanger Shepherd Density Meter and Calibrated Wedge. This instrument has been adapted to suit this special purpose, and can be obtained from the E.S.S. Colour Filter Co., by quoting "G.L.C. Standard." The test papers are prepared as follows:—"Waterlow's Bibulous" papers in 1¼ in. perforated squares are used, all water-marked pieces being rejected. They are soaked in a 6·5 per cent. solution of lead acetate, and drained and stored wet until required. Some time before use they are spread out in a large desiccator until nearly dry, and then transferred to a large glass vessel where they can be stored over water. When used, the water content of the paper should be such as would be attained if stored for an indefinite period over water at the temperature of testing.

The mean curve representing the variation of the density in terms of the volume of pure hydrogen sulphide (ml. at N.T.P. $\times 10^{-3}$) is

given in Fig. 8. The gas passed during the test should be such that the density of the stain is between 0·8 and 1·7 units, since over this range the calibration curve is nearly a straight line, and the sensitivity of the optical method is found to be greatest. The paper when removed from the instrument, is placed immediately in a vessel over calcium chloride, and shielded from the light. The density of the stain is read off against a calibrated wedge, using a similarly dried paper from the same batch as the comparison diffuser. The volume of pure hydrogen sulphide at N.T.P. can now be obtained from the curve given, and its concentration determined in "parts

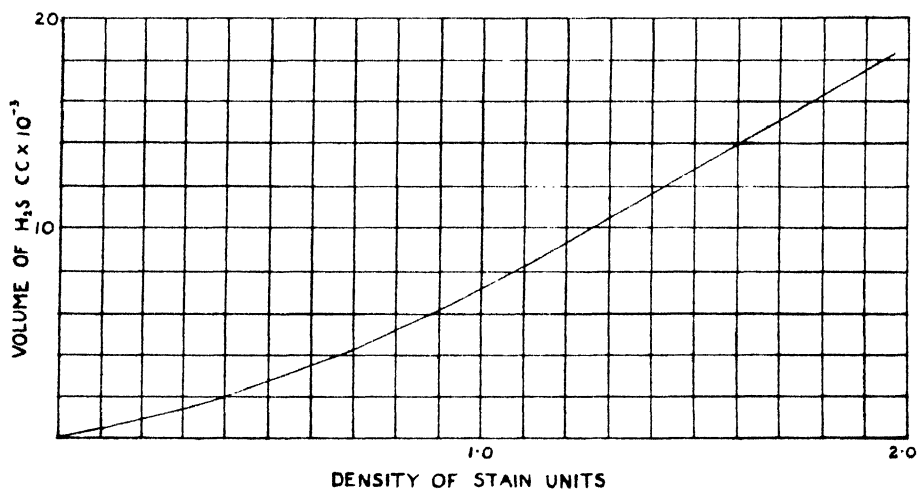



Fig. 8.

per million by volume of dry gas." The following relationship is useful in calculation :—

1 cu. ft. of gas at 60° F. and 30 ins. (sat.) = 26·4 litres (dry) at N.T.P.

Determination of Hydrogen Sulphide in Gas-Holder Water. The presence of soluble sulphates in the water of gas-holders is a potential source of hydrogen sulphide, which arises from the bacterial decomposition of these salts. In some cases, therefore, it is necessary to examine the holder water frequently for hydrogen sulphide.

Samples should be taken while the holder is full of gas, and from a point not less than 5 ft. below the surface. The bottles used for collecting samples should be free from air, and any contact between the sample and air should be avoided. The analysis should be carried out at once; if this is not possible, the sample should be stored in a cool dark place.

For analysis, a suitable volume of the water is taken, carbon dioxide bubbled slowly through it and led into the apparatus shown on p. 31.

The procedure is then identical with that described in the examination of coal gas. If necessary, a succession of papers may be used, but the operation must be continued until the last paper remains clean. The papers are then dried, their respective densities measured and converted into hydrogen sulphide equivalents. Fixed sulphide is determined, after the estimation of free hydrogen sulphide, by acidifying the water, and then repeating the test.

If x be the total volume of hydrogen sulphide in ml. $\times 10^{-3}$, and y be the volume of water in ml., then the concentration of hydrogen sulphide in the water is $106 \frac{x}{y}$ grains per 1000 gallons.

4. **Hydrocyanic Acid.**—This impurity may be the cause of serious corrosion of mains and fittings if left in the gas, and should be removed as completely as possible. Usually some 25 to 30 per cent. is extracted along with the ammonia, the remainder passing forward to the oxide purifiers, where it can be entirely removed if suitable precautions are taken.

The method of determination quoted in Vol. I., p. 314 (ii) is recommended with the following modifications. The final titration is carried out by adding the thiocyanate solution to a known volume of $N/10$ silver nitrate solution, using ferric alum as indicator. For this purpose, the thiocyanate solution is made up to 100 ml. and a preliminary titration carried out using a small volume of it, and titrating with $N/10$ silver nitrate solution until a permanent red colour is produced. The titration is then repeated, using such a quantity of $N/10$ silver nitrate solution as will require approximately 50 ml. of the thiocyanate solution.

An approximate value for the hydrocyanic acid content of the coal gas can be obtained by using the following rapid procedure. The hydrocyanic acid is absorbed as in the previous method, the gas being passed rapidly for a short period through the absorption bottles. The contents of the bottles are then mixed, made up to 100 ml., and 10 ml. taken for the determination. The solution is boiled for two minutes, acidified by the addition of 10 per cent. hydrochloric acid, and then boiled for a further one minute to coagulate the precipitated sulphur. The solution is then cooled, 2 ml. of a 6 per cent. ferric chloride solution added, and the solution filtered into a small Nessler cylinder. The colour is then matched against similar volumes of standard solution containing 2 ml. of the ferric chloride indicator and varying quantities of thiocyanate, and the HCN content of the gas calculated, 1 part CNS being equivalent to 0·466 parts HCN.

5. **Naphthalene.**—Coal gas from horizontal retorts and coke ovens is usually saturated with naphthalene, and according to the vapour pressure of this compound should contain some 4 grains per 100 cu. ft.

at 15°. Horizontal retort gas, however, usually contains considerably more naphthalene than is necessary for saturation, the excess, presumably being carried as a fine mist or fog which is difficult to remove by settling or further cooling. Gas from vertical retorts has been subjected to less cracking and contains only 1 or 2 grains of naphthalene per 100 cu. ft. The only satisfactory method for removing the naphthalene is to wash it out of the gas with suitable solvents. For the control of the extraction process, the naphthalene entering and leaving the washers must be determined, and also the naphthalene content of the wash oil. The determination of naphthalene in gas at varying temperatures is discussed fully in Vol. I., p. 315 *et seq.* The following details of procedure, based on these original methods, have been found to yield accurate results in actual gas works practice :—

Two wash bottles are employed for the extraction of the naphthalene, each containing about 50 ml. of alcoholic picric acid solution prepared by adding 1 part of alcohol to 4 parts of $N/20$ picric acid solution. The test is carried out over a period of twenty-four hours, and the rate of gas passed is varied inversely with the naphthalene content of the gas. When the naphthalene content exceeds 10 grains per 100 cu. ft., gas is passed at the rate of 0·25 cu. ft. per hour ; when the naphthalene content is approximately 5 grains per 100 cu. ft., the rate of gas flow is adjusted to 0·5 cu. ft. per hour. The gas is measured at the outlet of the absorption bottles by means of a wet meter. After completing the absorption, the contents of the bottles are filtered, and the precipitate redissolved in a few ml. of alcohol, the filter paper being washed with a further small volume of alcohol. Both the washings and the alcoholic solution of naphthalene picrate are collected in a beaker and diluted with five times their volume of $N/20$ aqueous picric acid solution.

The precipitated naphthalene picrate is filtered off on a Buchner funnel. After slight washing with 1 per cent. picric acid solution, the filter paper is removed and pressed between folds of blotting paper until no fresh yellow stain is produced after five minutes' pressure. The filter paper is then transferred to a beaker containing about 220 ml. of distilled water and boiled, the boiling being continued for a few minutes after the smell of naphthalene has disappeared. The dissociation of the naphthalene picrate is usually complete in about ten minutes. The paper is then removed from the solution, the adhering picric acid being washed back into the beaker by means of distilled water. The contents of the beaker are then titrated whilst hot with $N/10$ sodium hydroxide solution, using cochineal as indicator.

An allowance must be made for the picric acid retained by the filter paper after pressing. This can be taken as equivalent to 0·1 ml.

N/10 sodium hydroxide solution or approximately 0·2 grain naphthalene. The exact quantity should, however, be determined periodically.

The naphthalene content is expressed in grains per 100 cu. ft. of gas (corrected) and is calculated from the expression :—

$$1 \text{ ml. } N/10 \text{ NaOH} = 0{\cdot}0128 \text{ g. } C_{10}H_8.$$

Note.—There are probably small quantities of other volatile hydrocarbons besides naphthalene present in coal gas which are capable of giving a precipitate with picric acid. In the above test any such compounds are expressed as " naphthalene."

Estimation in Warm Crude Gas. The gas is collected by passing it through a tar filter, and then through a short lagged sampling tube into the absorption vessels. The assembly of the apparatus in

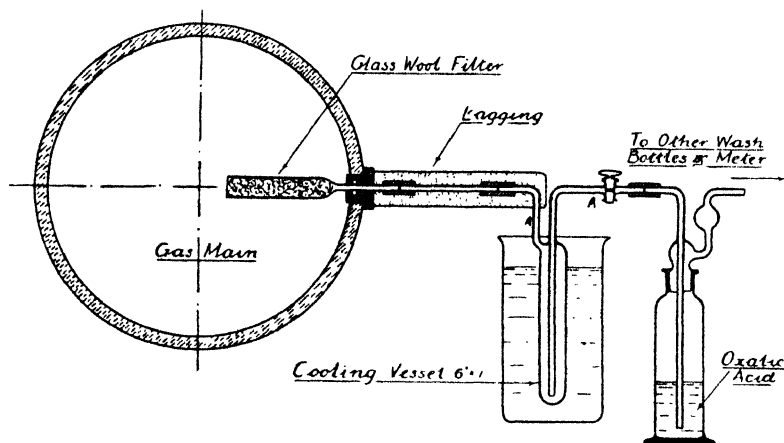



Fig. 9

relation to the gas main is shown in Fig. 9, and it is essential that the strict conditions of lagging and cooling should be fulfilled. The gas passes from the condensing vessel through two wash bottles, each containing 100 ml. of a saturated solution of oxalic acid, then through a wash bottle containing 100 ml. of *N*/20 picric acid solution, and finally through a wet gas meter for measurement. The rate of flow of gas is maintained at 0·5 cu. ft. per hour over a period of eight hours. The naphthalene which is deposited in the delivery tube A and the condensing vessel is dissolved in a small volume of alcohol and precipitated in excess *N*/20 picric acid solution. The oxalic acid solution is then transferred to a wide-necked flask fitted with a cork and a long and short glass tube, and a slow stream of air is bubbled through the solution, which is maintained at a temperature of 80° to 100° during the passage of the air. The naphthalene evolved is collected in two wash bottles, the first containing 100 ml. of standard alcoholic picric acid solution and the second 100 ml. of *N*/20 aqueous

picric acid. At the end of two hours, the first bottle is replaced by one containing 50 ml. of *N*/20 picric acid solution and is, when necessary, replaced by similarly charged bottles until the evolution of naphthalene is complete. The several solutions containing naphthalene picrate are finally mixed and filtered, and the naphthalene determined as described above, but without reprecipitation.

The Determination of Small Quantities of Naphthalene. When only small quantities of naphthalene are present in the gas, it can be determined by direct absorption in aqueous picric acid. Two wash bottles, each containing about 50 ml. *N*/20 picric acid solution, are employed, the gas being passed at the rate of 1 cu. ft. per hour for twenty-four hours. The naphthalene picrate obtained is filtered off, dissolved in a few ml. of alcohol, and reprecipitated with *N*/20 picric acid solution. The determination then proceeds as before.

6. **Organic Sulphur Compounds.**—After the removal of the above impurities there are still present some 20 to 30 grains per 100 cu. ft. of sulphur compounds, of which carbon disulphide constitutes some 70 to 80 per cent., the remainder being thiophene, mercaptans, etc. In the Carpenter-Evans process adopted by The South Metropolitan Gas Company, the gas, preheated to 300°, is passed over a nickel catalyst to convert these compounds into hydrogen sulphide, which is subsequently removed. In this way the total sulphur is reduced to 6 to 8 grains per 100 cu. ft. Washing the gas with oil for the removal of the benzole (see p. 38) removes some of the sulphur, the quantity depending upon the quantity of wash oil per unit volume of gas. The following figures illustrate this aspect (Hollings [1]) :—

Gallons Wash Oil per 1000 cu. ft. of Gas.	Percentage Sulphur Removed in Rotary Washer.
10	37
15	45
25	64
30	73

Some 8 gallons of oil per 1000 cu. ft. are usually employed and hence the sulphur left in the gas is about 20 grains per 100 cu. ft.

By the use of active carbon for benzole removal, a considerably greater sulphur absorption is possible, and a reduction to some 6 to 8 grains per 100 cu. ft. is average practice.

It is usual to determine the sulphur compounds collectively, a "total sulphur" figure being obtained. For the determination of the total sulphur in town's gas a standard test is prescribed by the Gas Referees, for details of which see Vol. I., p. 308 and General Notification of the Gas Referees, 1934. A more rapid method,

[1] *Chem. and Ind.*, 1934, 143.

especially suitable for works control testing, is that of Somerville, described in detail in Vol. I., p. 312.

Carbon disulphide is rarely determined separately, but if required, the estimation can be carried out as described in Vol. I., p. 307. The Harcourt method (Vol. I., p. 308), when modified as described below, has been found to yield satisfactory results, but it should be noted that traces of other sulphur compounds may be decomposed by the platinised pumice, and therefore the figure obtained is not strictly accurate as a measure of the carbon disulphide content of the gas. The apparatus employed is similar to that illustrated in Vol. I., p. 307, gas being passed through the Harcourt flask, heated to 420°, at 0·5 cu. ft. per hour for twenty-four hours. The gas leaving the flask is passed through two wash bottles, each containing 100 ml. of 10 per cent. sodium hydroxide solution, and then through a meter fitted with a governor. When the absorption is complete, the contents of the bottles are washed out, and the sodium sulphide which has been formed is oxidized in the cold by means of sodium peroxide or bromine. After boiling the solution, the sulphur content is determined by precipitation as barium sulphate in the usual manner. The results obtained are expressed as grains of sulphur per 100 cu. ft. of gas.

7. **Water Vapour.**—Although hardly classifiable as an impurity, water vapour is often removed from coal gas to reduce the corrosion of mains and services, and also to obviate the necessity of removal of condensed water by frequent pumping of syphons at various points in the supply system. Dehydration is effected by washing the gas with a concentrated aqueous solution of glycerine or of calcium chloride. To ascertain the efficiency of the process, the moisture content of the gas must be determined before and after the washer. The following apparatus, designed by The Gas Light and Coke Co., may conveniently be used for the measurement of the dew point of the gas. This is shown in Fig. 10, and is supplied by Messrs Scientific Supplies Ltd., 52 Hatton Garden, E.C. 1. Gas under test passes over the dry bulb thermometer T^1 in tube A, and thence over the wet bulb thermometer T'' in tube B. The constriction at F prevents diffusion of water vapour backwards. The gas then passes to tube C and is finally burnt at E which acts as a fixed orifice. The level of water in tube D then represents a known rate of flow. Before using the hygrometer, the gas supply is disconnected and distilled water is delivered into C by means of a pipette through D until the wet bulb is covered with water, care being taken to prevent water from entering A. After a few minutes, water is removed from C by the attachment of a piece of rubber tubing to D, until the level remains just below L. Gas is then admitted to the apparatus until the pressure indicated by the gauge tube D is about 1 in. The gas is then lighted at E, and after a few minutes

the pressure is regulated until the required pressure is shown on the gauge. This is the pressure, previously found necessary by calibration, to pass exactly 5 cu. ft. per hour through the apparatus. The burner should be lighted at least ten minutes before observations are taken, after which temperature readings of both thermometers are taken at half-minute intervals until a set of four consecutive readings is obtained, differing by not more than 0·05° F. The readings of each thermometer

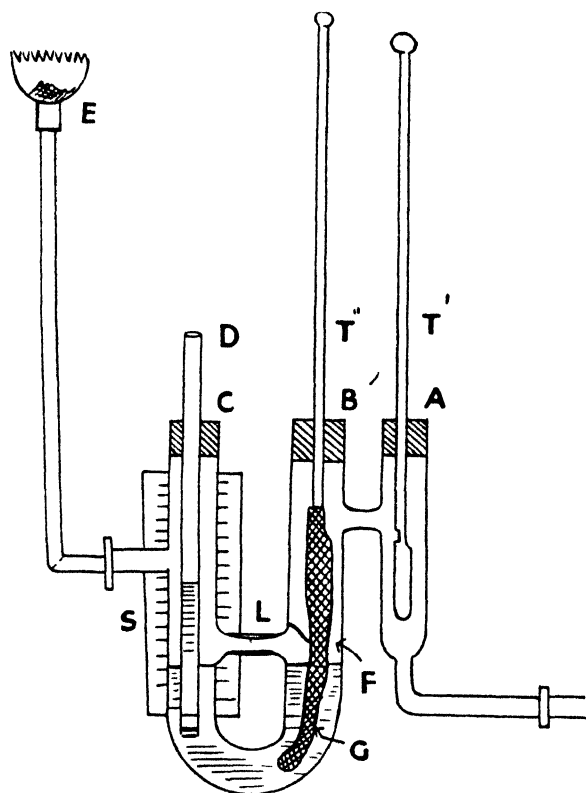



Fig. 10.

(after correction for calibration errors) are averaged. The following simplified formula may be used for the calculation of vapour pressure of water in the gas at the dew point :—

$$P = P^1 - 0{\cdot}42\,(T - T^1),$$

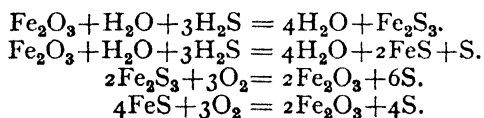
Where P^1 = vapour pressure (mm.) at the temperature of the wet bulb.
T = Temperature of dry bulb, °F.
T^1 = Temperature of wet bulb, °F.

8. **Benzole.**—The extraction of benzole from coal gas, and its subsequent rectification and use as motor fuel is largely practised. In most works the benzole is washed from the gas, using gas oil, creosote

or other tar fractions. An alternative method is to pass the gas through active carbon. The quantity of benzole which can be extracted is determined primarily by the type of carbonizing plant employed. From horizontal retorts or coke ovens, up to 3 gallons per ton may be recovered. With continuous vertical retorts, however, lower yields of about 2 gallons and under are customary. The crude benzole recovered is a mixture of benzene, toluene, xylene, carbon disulphide, paraffinoid hydrocarbons, etc., and hence the determination of benzene by ordinary methods of gas analysis is of little value for process control. It is customary to wash a sample of the gas in a pilot apparatus, using the same oil and maintaining the same temperature conditions as in the large scale plant. This test is applied to the gas before and after leaving the washer. The crude benzole is recovered from the wash oil by steam distillation, the degree to which the oil is stripped being controlled by the composition of the crude light spirit. Subsequently the crude benzole is refined by washing with sulphuric acid to remove the bases and unsaturated hydrocarbons, and finally with alkali for the removal of any phenolic constituents, etc. Details of the analyses of crude and refined benzole are given on pp. 207-286.

Oxide Purification

The removal of hydrogen sulphide from coal gas is usually effected by passing the crude gas through layers of iron oxide. Ferric and ferrous sulphides are formed, which on exposure to air are decomposed, the oxide being re-formed and sulphur liberated, *i.e.*—

$$Fe_2O_3+H_2O+3H_2S = 4H_2O+Fe_2S_3.$$
$$Fe_2O_3+H_2O+3H_2S = 4H_2O+2FeS+S.$$
$$2Fe_2S_3+3O_2 = 2Fe_2O_3+6S.$$
$$4FeS+3O_2 = 2Fe_2O_3+4S.$$

The gas is usually passed through four purifier boxes containing two or more layers of oxide. The majority of the hydrogen sulphide is removed in the first two boxes, the subsequent boxes taking out the traces so that there is less than 1 part per million cu. ft. at the outlet of the final box. From time to time, as their contents become sulphided and inactive, the boxes are emptied and recharged with fresh material. In order to reduce the frequency of this operation, a small amount of air is added to the gas so that in the final boxes the oxidation process takes place *in situ*. For efficient working the order of the boxes must be changed periodically, so that as each box becomes sulphided it is placed at the end of the series where the sulphide is reconverted to the oxide. In this way the mass can be worked up to some 60 per cent. of sulphur. For the analysis of spent oxide, see p. 40.

The quantity of air added to the gas must be carefully controlled as the revivification reaction is exothermic. Further, the nitrogen introduced in the air is a useless diluent. It is good practice to add some 1·5 to 2 per cent. of air, assuming that the gas contains initially 0·2 to 0·3 per cent. of oxygen. The oxygen content of the gas should be tested at frequent intervals before and after the purifiers. For this purpose the usual Orsat apparatus may be used, although the accuracy is hardly sufficient for the small amounts of oxygen present. Preferably the Haldane apparatus should be used (see Vol. I., p. 289 *et seq.*). The hydrogen sulphide content of the gas entering the first purifier, and leaving this and the subsequent boxes, should be periodically measured. For this purpose Somerville's method, Vol. I., p. 305, may conveniently be used. In the gas leaving the final purifier, hydrogen sulphide is present to the extent of under 1 part per million cu. ft., and it is customary to test the purity of the gas at this point by the time required to stain a lead acetate paper. The Standard Gas Referees Test may be applied.

SPENT OXIDE

Sampling.—As with fresh oxide, the composition of the spent material may vary considerably throughout the mass, and to obtain a representative sample, the procedure given in Vol. I., p. 4 *et seq.* must be adhered to. The final sample representing a parcel of spent oxide is usually stored in a number of sealed 4-oz. bottles, and one of these samples is taken for analysis. Prior to analysis, the oxide is ground in a mortar or in a small hand-mill, so that the whole of it passes through a No. 14 B.S.S. sieve.

1. **Moisture.**—10 g. of the sample is dried for three hours in a water oven maintained at 100°. The loss in weight is taken as the amount of "free moisture" in the sample. In addition to the loss of water, some of the cyanide compounds present may undergo decomposition at this temperature, with loss of hydrocyanic acid. Spent oxide, thus dried, must not be used for the estimation of cyanides. Slight losses due to tarry compounds and sulphur are also included in this figure as they volatilise slowly at 100°. The errors arising from these factors are, however, small, and the figure obtained is sufficiently accurate for control purposes.

2. **Sulphur and Tar.**—In carrying out this determination, it should be remembered that the method employed is a conventional one, yielding a value for material soluble in carbon disulphide rather than a direct free sulphur figure. It yields, however, results of sufficient accuracy for ordinary purposes, and is generally recognised as a basis for the buying and selling of spent oxide.

The dried oxide from the moisture determination is extracted by means of freshly distilled carbon disulphide in an ordinary type of Soxhlet apparatus designed to take a filter paper thimble 22 mm. × 80 mm. This thimble rests upon a plug of glass wool, which raises the top of the thimble slightly above the level of the syphon tube, so that any particles of oxide which are accidentally carried over the top of the thimble will be filtered off as the carbon disulphide passes to the syphon. Before commencing the extraction, the clean flask of the extraction apparatus is dried in a water oven at a temperature of 100° for half an hour, cooled and weighed. The extraction is continued so long as the condensed carbon disulphide returning to the flask shows any coloration due to sulphur or tar. The time taken for this will depend upon the tar content of the spent oxide. Thirty minutes after the liquid returning to the flask is considered colourless, the flask is disconnected so that one or two drops of the condensate returning to the flask may be collected on a watch-glass. If the extraction is complete, the carbon disulphide will evaporate without leaving any residue.

When the extraction is complete, the solvent is distilled off, the flask blown out with dry air, and dried for two hours at 100° in a water oven. The flask is finally cooled and weighed. The increase in weight gives the weight of sulphur plus tarry matter.

The dried extract is then digested with 20 ml. of concentrated sulphuric acid for several hours at a temperature of 100°. The period of digestion for the complete decomposition of the tar will depend on the quantity of tar present in the carbon disulphide extract. When more than 2 per cent. of tar is present, it is advisable to digest over-night in the water oven. About 300 ml. of water is then added, and the sulphur is filtered off and washed with hot water until free from sulphates and soluble organic matter. The filter paper and contents, after drying, are placed in a Soxhlet thimble and extracted with carbon disulphide for two to three hours. The excess carbon disulphide is then removed as before and the flask dried and weighed. The difference between the weight of the first extract and that of the second gives the weight of tarry matter soluble in carbon disulphide.

If the tar amounts to more than 4 per cent. it may be necessary to repeat the sulphuric acid treatment before pure sulphur can be obtained. The necessity for this will be indicated by the dark colour of the sulphur on first treatment, and by the difficulty experienced in removing the first portion of spent sulphuric acid by filtration.

Boot and Ward [1] recommend a method of estimating sulphur and tar which, they state, is more rapid and yields more accurate results than the carbon disulphide extraction method. The method depends

[1] *Chem. and Ind.*, 1935, **54**, 116.

on the quantitative conversion of sulphur into sodium thiosulphate by refluxing the oxide with sodium sulphite solution. The excess sulphite present is then rendered inactive by the addition of formaldehyde and acetic acid, and the thiosulphate is determined by titration with standard iodine solution in the presence of starch. Any ammonium thiocyanate which is present in the oxide will tend to react with the iodine solution, but it was found that its effect was negligible under the conditions of the estimation. The residual material, after the removal of the sulphur as thiosulphate, is extracted with carbon disulphide in order to determine the tar content.

3. **Ammonia.**—10 g. of the oxide is introduced into the distilling flask of the apparatus shown on p. 69. 5 ml. of 10 per cent. caustic soda solution is added, and the ammonia is then distilled off into 50 ml. of $N/10$ sulphuric acid solution. When the distillation is complete, the excess of acid present in the distillate is determined by titration with $N/10$ caustic soda solution, and the percentage of ammonia calculated in the usual way.

4. **Iron.**—5 g. of the original oxide is weighed into a silica crucible, dried for two to three hours in the water oven, and then ignited over a Meker burner for one hour. The crucible and its contents are then placed in a 500 ml. beaker, 250 ml. of aqua regia is added, and the solution boiled for two to three hours. The percentage of iron in the solution is then determined by the method described under the analysis of new oxide.

5. **Naphthalene.**—10 g. of the original oxide is placed in a small flask together with 100 ml. of 90 per cent. alcohol. The flask is corked, agitated, and allowed to stand for three or more hours at 30°. The liquid is then filtered into a larger flask and the filter washed once or twice with 90 per cent. alcohol; 400 to 500 ml. of strong picric acid solution is then added, the flask well agitated and allowed to stand a short time. The naphthalene picrate which separates out is filtered and washed into a flask with the smallest quantity of strong picric acid solution. Absolute alcohol is added in sufficient quantity to dissolve the precipitate, and then $N/20$ picric acid solution is added in excess. The quantity of naphthalene present is then determined as described on p. 277.

6. **Cyanogen Compounds.**—The greater part of the hydrocyanic acid present in coal gas is absorbed in the oxide purifiers, where it combines with the iron to form ferrocyanides. As ammonia is usually present, these compounds may contain ammonia in the molecule. In addition, thiocyanates are present, generally as ammonium thiocyanate. If the ferrocyanide is sufficiently high, the spent oxide may be sold on this basis as it is then profitable to extract these compounds. For the determination of the ferrocyanides—collectively known as prussian

blue—the Knaublauch method is generally used. For details of this and other methods, see Vol. I., p. 652 *et seq.*

IV. PRODUCTS OF CARBONIZATION

The products of the carbonization of coal are considered under the following headings :—

A. Coal gas.
B. Tar and tar products.
C. Ammonia products.
D. Coke.

A. Coal Gas

After removal of the various impurities which are discussed in the preceding section, the gas is ready for distribution, its composition varying only in the differing proportions of the constituent gases. In the following table are given typical analyses of town's gas as distributed in different localities.

	Analysis.							Specific Gravity.	Calorific Value. B.Th.U. per cu. ft.
	CO_2.	O_2.	C_nH_m.	CO.	H_2.	CH_4.	N_2.		
London—A .	1·5	0·2	3·8	7·6	52·1	27·8	7·0	0·419	562·5
B .	2·6	0·6	3·3	12·7	49·4	23·3	8·1	0·450	502·0
Provincial—A .	3·7	0·6	1·9	17·4	51·4	19·1	5·9	0·465	459·0
B .	3·0	0·4	3·0	20·0	46·0	19·5	8·1	0·505	477·9
C .	3·3	0·4	2·8	8·4	50·7	25·7	8·7	0·426	508·3

The admixture of water-gas increases the carbon monoxide and hydrogen content, while the manufacture of gas in continuous vertical retorts, etc., to which steam is admitted, also increases these constituents as compared with gas from horizontal retorts or coke ovens. The influence of the temperature of carbonization and the degree of cracking on the composition of the gas, and in particular on the hydrogen and unsaturated hydrocarbon content, has been already discussed.

The percentage of non-combustible or inert gases in town's gas should be carefully controlled since these have no heating or illuminating value, and are useless diluents. Further, the oxygen content should be kept as low as possible so as to reduce the rate of corrosion of mains and fittings, etc.

Methods of Analysis.—For the complete analysis of coal gas, the Bone and Wheeler apparatus is generally used in this country. Carbon dioxide, carbon monoxide, oxygen and unsaturated hydrocarbons are determined by absorption, and the hydrogen and saturated hydrocarbons by explosion or by combustion over platinum or copper oxide.

The nitrogen is then obtained by difference. A full description of the above apparatus is given in Vol. I., p. 285 *et seq.* For details of the reagents employed for the absorption of the above constituents, see Vol. I., pp. 242-247, and for methods of determining hydrogen and methane by combustion, see pp. 248-263. The saturated hydrocarbons are generally expressed as methane although some ethane is usually present. The estimation of methane and ethane (and other saturated hydrocarbons) is discussed in Vol. I., p. 251.

The unsaturated hydrocarbons present consist mainly of ethylene, benzene and small proportions of the homologues of these compounds. Ethylene may be estimated by absorption in bromine as described in Vol. I., p. 297. Benzene may be calculated from the total volume of unsaturated hydrocarbons, as determined by absorption in bromine or sulphuric acid, less the percentage of ethylene as determined above. Other methods of estimation are given in Vol. I., p. 298. The volume of benzene and toluene which is available for extraction by oil washing is generally obtained by passing a sample of the gas through the wash oil which is to be used. By the distillation of the oil, the mixture of crude benzol, toluol, etc., can be separated and measured. This method is discussed on p. 238. Where it is desired to determine the relative proportions of the different unsaturated hydrocarbons, the method devised by the Fuel Research Board [1] may be used. This consists essentially in the separation of the unsaturated gases as their bromine derivatives and the regeneration of the ethylene, propylene and butylene from these compounds by the action of a zinc-copper couple. Condensible hydrocarbons (benzene, etc.) are first removed from the gas by scrubbing with oil. The following is a typical analysis of the unsaturated hydrocarbons from town's gas :—

	Per cent.
Condensible vapours	0·50
Ethylene	1·90
Propylene	0·28
Butylene	0·08
Butadiene	0·02
Unaccounted for	0·12
	2·90

Owing to the small quantity present, it is often convenient to determine oxygen in the Haldane apparatus, which is especially designed for estimating small quantities of gases. (See Vol. I., pp. 289 and 301).

In gasworks practice, the total inert content of town's gas is frequently determined, and this necessitates the estimation of the nitrogen content. In the ordinary way this is obtained by difference after the rest of the

[1] *Fuel Research Technical Paper*, No. 19, 1928.

constituents have been determined. To avoid the complete analysis of the gas, the nitrogen can be conveniently estimated in the Metrogas apparatus by combustion over copper oxide and absorption of the resulting gases. For details of this, see Vol. I., p. 295.

Calorific Value and Specific Gravity of Gas Manufactured

Statutory Companies supplying coal gas for distribution are under obligation to maintain the calorific value of the gas to within 5 per cent. of a declared value. There is no restriction as regards the calorific value which may be adopted by a Gas Undertaking, and values varying from 400 to 560 B.Th.U. per cu. ft. are found, the majority of Undertakings supplying gas of 450 to 500 B.Th.U. per cu. ft. While there are no regulations regarding the specific gravity of the gas supplied, this characteristic is of importance as it influences the quantity of air injected in the bunsen burner. In the majority of gas appliances the air for combustion is entrained by the use of the bunsen burner principle, and any change in specific gravity of the gas will alter the proportions of air and gas and may necessitate readjustment of the apparatus to maintain efficient combustion.

In order to be able to supply consistently a gas of any declared value, it is necessary to control the composition of the gas as evolved from the retorts. There are two main methods of carbonization—intermittent and continuous. In the intermittent processes as exemplified by the horizontal retort, the calorific value of the gas rises to over 600 B.Th.U. per cu. ft. immediately after charging the retort, and falls ultimately to about 300 B.Th.U. per cu. ft., the final gas consisting mainly of hydrogen.

The specific gravity varies correspondingly with the calorific value, falling at the end of the period, when hydrogen alone is being evolved. In the continuous process, as in the Glover-West, Woodall-Duckham and other vertical retorts, the calorific value of the gas remains fairly constant so long as the coal is passed through the retort at a more or less uniform rate. With intermittent charging, as with horizontal retorts, it is impossible to produce a constant calorific value from a single retort, but as there are always a number of retorts in use, it is possible, by charging them at different times, to reduce considerably the periodic change in calorific value. Thus the greater the number of retorts in use, the smaller is the variation in gas quality. Immediately after charging, the gas is very rapidly evolved from the retort and would cause considerable pressure if no steps were taken to facilitate its removal. It is therefore the practice to extract the gas from the retort by suitable exhausting machinery, and this allows additional control of the calorific value. The fireclay retorts employed

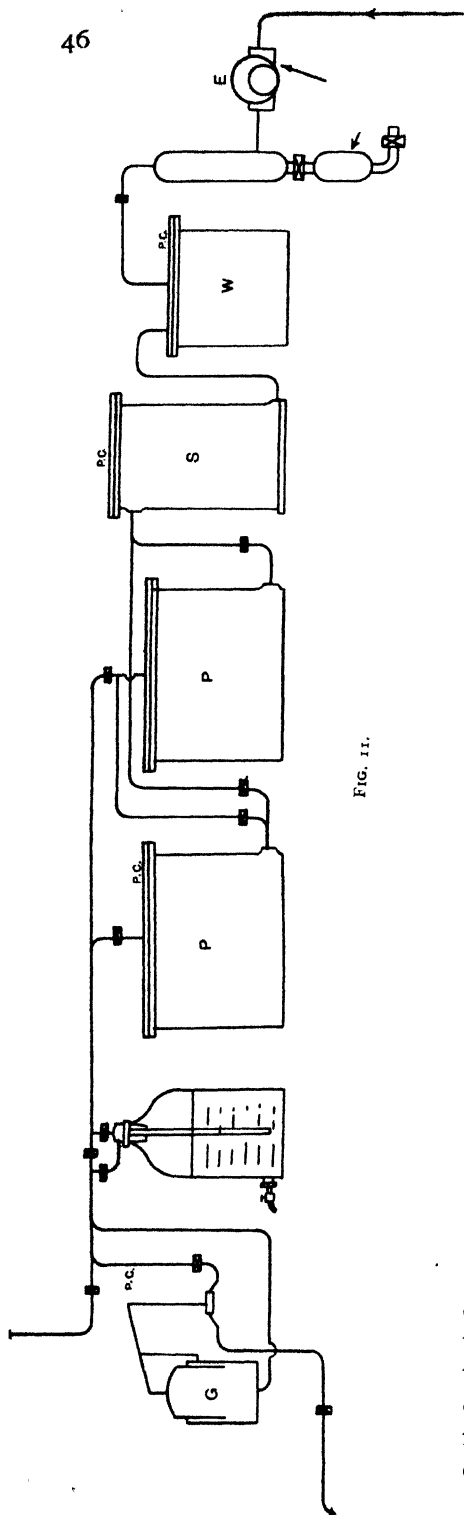



Fig. 11.

are not gas-tight and any vacuum in the retort results in flue gases being entrained into the gas. This reduces the calorific value of the gas. It is the practice, therefore, to reduce the vacuum on the retorts when the rate of gas evolution falls off, the vacuum being again increased after recharging. In many works, where the gas is distributed at a calorific value of under 500 B.Th.U. per cu. ft., inert gas is deliberately entrained by the use of excessive vacuum in order to reduce the calorific value to the required figure. Using a first-class gas coal, the calorific value of the gas, when no inert gas is added, varies from 560 to 650 B.Th.U. per cu. ft. The practice of reducing the calorific value by the addition of large proportions of inert gas is to be deprecated, as the inert gas must be passed through the purifying system, gas holders and mains, which must be correspondingly larger than if a gas of higher calorific value had been produced. It is obvious that some gas of lower calorific value must be available for dilution and control purposes, and in many works it is the practice to make water-gas which is mixed with the coal gas to give the required calorific value. Alternatively, producer gas may be added to the coal gas, a practice which is frequently adopted. Whatever method be employed, a continuous record of the calorific value of the gas leaving the retorts is advisable. When dealing with the crude gas direct from the retorts, it is necessary to clean and purify the gas before it

enters the recording calorimeter. Fig. 11 illustrates a typical small-scale purifying apparatus used for this purpose.

The crude gas is drawn from the vacuum main through condensers by a small exhauster (E), and, after cooling, passes through a sulphuric acid washer (W) to remove ammonia, followed by a scrubber (S) which is filled with loose packing, and thence through two oxide purifiers (P). Finally the naphthalene is removed by passing through a wash bottle containing picric acid solution. By means of a small governor (G) the surplus gas can be returned to the vacuum main, the clean purified gas being led to the calorimeter as required.

Calorific Value.—The standard apparatus for the measurement of the calorific value of the purified gas is the Boys calorimeter, which is approved by the Gas Referees for this purpose. Details of this apparatus are given in Vol. I., p. 352.

In the place of the ordinary type of test meter as shown in Vol. I., p. 355, a new type of meter has been designed by Professor Boys and is known as the Bell meter. This meter has a capacity of $\frac{1}{12}$ cu. ft. per revolution and consists of a tinned copper drum mounted on bearings within a spun copper bowl, and surmounted by a glass bell. Readings are taken on a scale on the periphery of the drum with reference to a fixed sight. In this way no spindle and gland through the casing of the meter are necessary. There are many advantages in the use of this meter. For further details, see *Gas Calorimetry*, Mills & Hyde, London, 1932.

Another more recent development in calorimetry is the Boys Box calorimeter, which is also officially recognised by the Gas Referees. There are many other types of calorimeters which may be used for the measurement of the calorific value of gases, and for details of these reference should be made to *Gas Calorimetry* (*loc. cit.*). In regard to the use of Boys's calorimeter, a standard method of testing is specified by the Gas Referees, which must be employed by gas examiners when determining the calorific value of town's gas under the provision of the Gas Undertakings Acts of 1920 and 1929. The method employed is briefly as follows, while for full details reference should be made to the General Notification of the Gas Referees (1934).

1. The testing apparatus is checked for soundness in the manner prescribed.
2. The capacity of the meter is verified by the use of a $\frac{1}{12}$ cu. ft. measure.
3. The gas is lighted and the flame observed for the correct shape.
4. The gas and water flows are adjusted as follows :—

Gas. Calorific Value.	Time for one rev. of the meter hand.
Not less than 540 B.Th.U./cu. ft.	70 to 85 secs.
Between 540 and 440 B.Th.U./cu. ft.	60 ,, 75 ,,
,, 440 ,, 340 ,, ,,	50 ,, 65 ,,

Water.

Calorific Value.	Volume of water for four revs. of the meter hand.
Not less than 540 B.Th.U./cu. ft.	2000 to 2400 ml.
Between 540 and 440 B.Th.U./cu. ft.	1800 ,, 2200 ,,
,, 440 ,, 340 ,, ,,	1600 ,, 2000 ,,

An interval of not less than forty-five minutes is allowed after the starting of the calorimeter before a reading is taken. The rate of flow of the gas is recorded by observing the time of one revolution of the meter hand. The temperature of the water should be lower than that of the surrounding air by not more than 5°. The water to the measuring vessel is switched over when the pointer crosses the 100 mark of the $\frac{1}{12}$ cu. ft. meter. While the water is collecting, the outlet thermometer is read at every quarter of the meter hand until fifteen readings have been taken. The inlet thermometer is read at each revolution of the meter except the last. At the end of four revolutions of the meter the water is switched back to waste and the water collected is thoroughly stirred and its volume recorded. The temperature is taken and the correction applied for apparent expansion of water in glass as follows:—

Below 18·5°	Subtract 0 thousandths.
18·5 to 23·5°	,, 1 ,,
23·6 ,, 28·0°	,, 2 ,,
28·1 ,, 31·5°	,, 3 ,,
31·6 ,, 34·5°	,, 4 ,,
34·6 ,, 37·5°	,, 5 ,,
37·6 ,, 40·5°	,, 6 ,,

After making any correction required on the thermometer readings, the mean of the four inlet readings should be subtracted from the mean of the fifteen outlet readings, the difference multiplied by 11·976, by the number of kilogrammes of water collected, and by the gas volume factor, to correct to standard temperature and pressure. (Gas Volume Factors, Table I. of Appendix to the General Notification, are purchasable direct from H.M. Stationery Office. The logarithms of the Gas Volume Factors are similarly published.)

The difference in degrees Fahrenheit of the temperature of the effluent gas and that of the surrounding air is taken, and $\frac{2}{5}$ths of the result is added to the result previously found if the gas is warmer, or subtracted if the gas is cooler. The result so obtained is the gross calorific value in B.Th.U. per cu. ft. at 60° F. and at a pressure of 30 in. of mercury.

Recording Calorimeters.—The value of the recording calorimeter for indicating the variations in calorific value of the gas from the retort house has already been discussed. Further, certain types may now be used as official instruments for the measurement of the

quality of the gas supplied by a Gas Undertaking, and are capable of a high degree of reliability and accuracy. The Boys, Fairweather and Thomas calorimeters are officially approved in this country. The

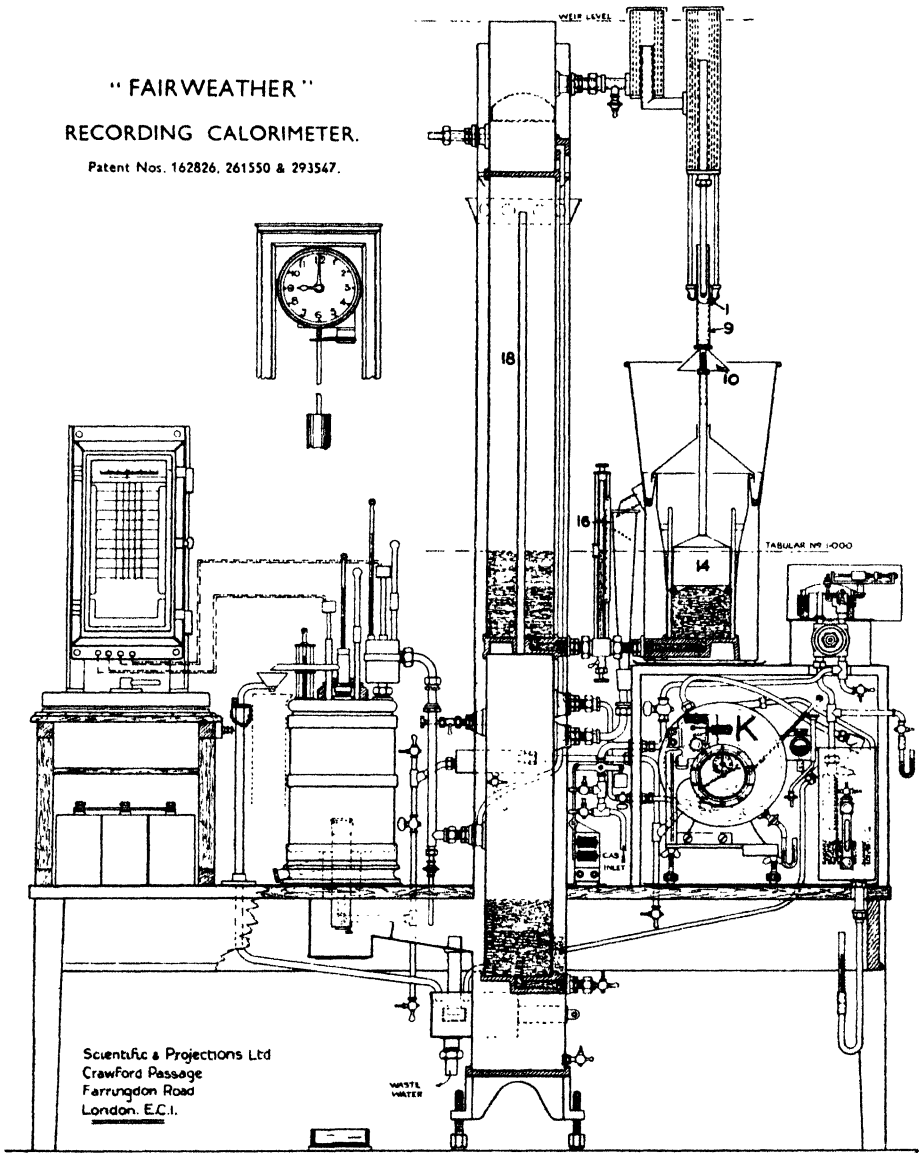



FIG. 12.

Fairweather instrument is based on the Boys calorimeter, while the Thomas calorimeter depends upon the change in resistance of an electrical circuit with alterations of temperature, resulting from changes

in the calorific value of the gas. The Fairweather instrument is the most widely used of these and will hence be described.

In this instrument (Fig. 12) the rise in temperature of the water which passes through the calorimeter is recorded directly in B.Th.U. per cu. ft. of gas burnt in the instrument. For this purpose it is obvious that constant rates of flow of gas and water must be maintained, and also that the instrument must be capable of automatically adjusting the gas flow according to the prevailing barometric conditions. The gas rate is maintained at 5 cu. ft. per hour by a special type of wet meter (K), the rate of rotation of which is controlled by an electro-magnetic form of escapement. The water flows from a constant head supply through an orifice (1), which is immersed in water in the vessel (9), from which it subsequently overflows. Vessel (9) is carried by a floating bell (14), the position of which is controlled by the volume of air in vessel (18), which is in turn dependent upon the pressure and temperature conditions. Vertical movement of the nozzle (1) increases or decreases the water rate in direct proportion to the change in density of the gas supplied to the calorimeter, and this automatically corrects the gas volume to standard conditions. In order to check the accuracy of this arrangement, the level of the oil which forms a seal between the chamber (18) and the vessel in which the float (14) is supported in the oil, may be read on a gauge (16), and any necessary correction applied. Water from a common source flows through the nozzle and thence to the calorimeter; it also passes through the water jacket of the meter and a heat interchanger to ensure that the gas and water are at the same temperature. The temperature of the water entering and leaving the calorimeter is measured by differential electrical resistance thermometers. These are connected to a bridge circuit, so that the out-of-balance current due to the difference in temperature may be recorded directly in terms of B.Th.U. per cu. ft. The above is a very brief description of the Fairweather calorimeter, which incorporates many interesting and ingenious devices, and for further details reference should be made to *Gas Calorimetry*, Mills & Hyde (*loc. cit.*).

Specific Gravity.—The principles involved in the measurement of the specific gravity of gases are discussed in Vol. I., p. 137 *et seq.* For control purposes, the specific gravity may be quickly determined by comparing the rates of effusion of gas and air respectively through an orifice (see Vol. I., p. 142). In the majority of the larger gas works a continuous record is advisable, and for this purpose the recording Gravitometer made by Alexander Wright & Co., Westminster, is frequently employed. The construction of the apparatus is shown in Fig. 13.

An aluminium bell (B) is suspended from one arm of a sensitive balance (A), the bell being sealed in an oil chamber (C). A stream

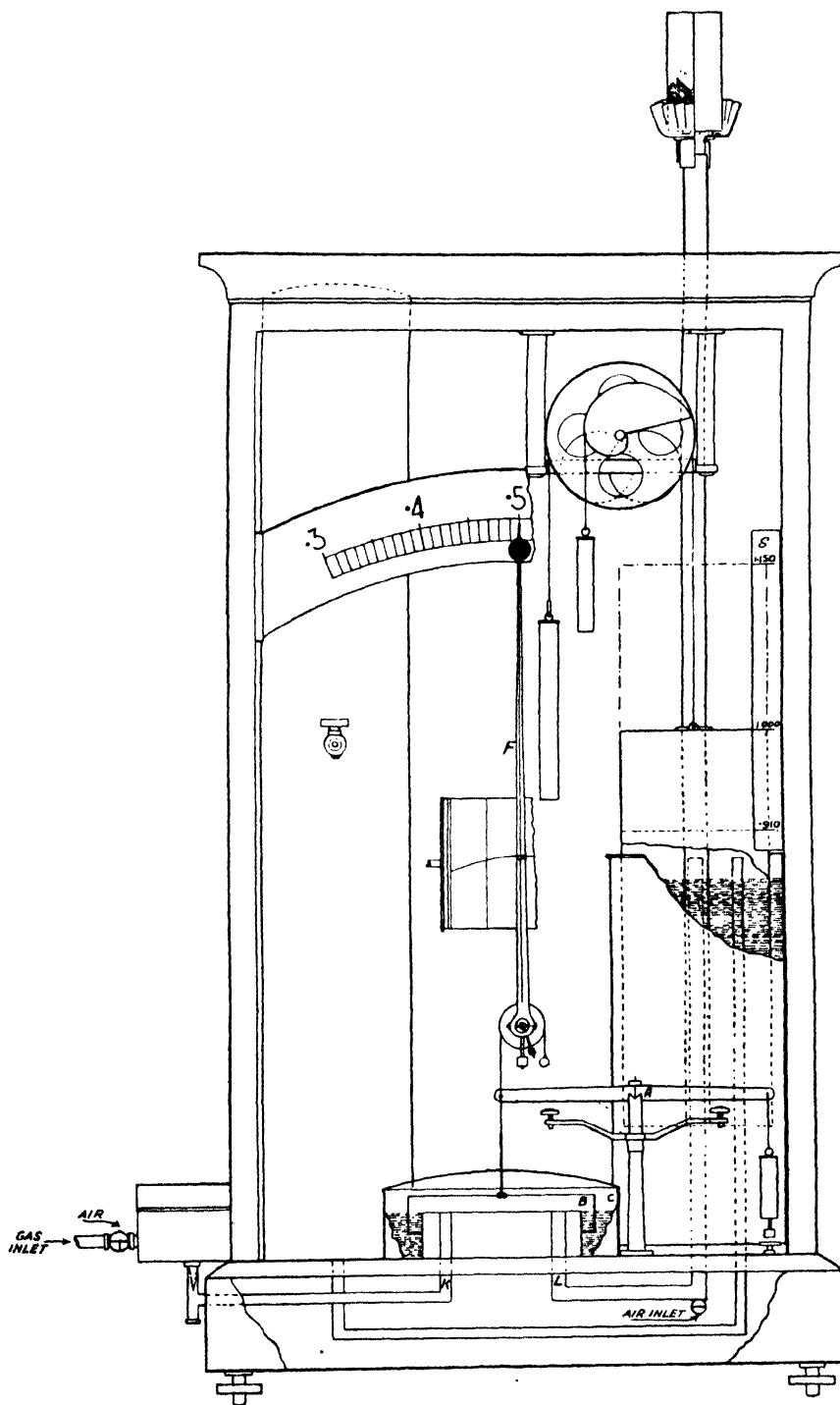



Fig. 13.

of gas is passed through the bell via the pipes (K) and (L) to a burner in which the gas is burnt. The bell is thus subject to a suction proportional to the difference in weight of the column of gas in the outlet pipe and that of an equivalent column of air. Any alteration in the specific gravity of the gas will cause a movement of the bell which is in turn transmitted to the pointer (F), which moves over a scale calibrated in terms of specific gravity relative to air. Any change in barometric conditions would introduce an error if the gas outlet pipe were of a constant length. A compensating arrangement is therefore provided by means of which the length of this pipe alters according to the atmospheric temperature and pressure. A constant weight of air and gas is thus preserved.

Illuminating Value.—Prior to the introduction of the thermal basis of charge for coal gas in 1930, the illuminating power of the gas was the only control of quality which was exercised on behalf of the gas consumer. The determination of the illuminating power was rendered redundant by the thermal basis of charge and has now little practical significance, as the majority of gas is consumed in burners equipped with incandescent mantles.

The illuminating value of different types of gas lighting appliances is of the greatest importance, and the measurement of this characteristic together with the thermal efficiency of the gas heating appliances—of which there is a large and ever-extending list—has been responsible for the evolution of a large number of tests and analytical methods—both physical and chemical. The discussion of these methods is beyond the scope of this volume, and for further details reference should be made to the following :—

The Science and Practice of Gas Supply, A. Coe, Halifax, 1934.
Domestic Utilization of Gas, N. S. Smith and R. N. Le Fevre, London, Walter King Ltd.
Theory of Industrial Gas Heating, P. Lloyd, London, Walter King Ltd.
" Modern Research Work and its Application in Practical Gas Supply," F. C. Smith, *Gas Journal*, **208**, 268, 363, 439.

Estimation of Gum in Coal Gas.—The adoption of processes for the removal of naphthalene and in some cases water vapour from coal gas, has materially reduced the interference with gas supplies due to deposits of these constituents. In some districts, however, a new difficulty has arisen due to the deposition from the gas of fine particles of gum which tend to accumulate in the jets of pilot lights, governors and such sensitive apparatus. It has been suggested that formerly this gum was largely deposited in the pipes, etc., along with the naphthalene and water and so did not pass forward to cause obstruction in the various gas appliances.

The gum deposited in the gas distribution systems of English works is formed by the interaction of small quantities of nitric oxide, oxygen and unsaturated hydrocarbons such as butadiene and cyclopentadiene. A rather different type of gum has been identified in gas distribution systems in America where water gas alone is being used and to which the term " liquid phase gum " has been given to distinguish it from the " vapour phase gum " formed by the interaction of nitric oxide and hydrocarbons. The " liquid phase gum " is not nitrogenous and results from polymerisation of liquid unsaturated hydrocarbons deposited from the water gas. Most of the nitric oxide is derived from waste gases drawn into the retorts and to in-leakage of air through mouthpieces which forms some nitric oxide on combustion. The quantity may vary greatly ; thus in fourteen works employing various methods of carbonization, the nitric oxide content of the unpurified gas varied from 0·3 to 4·7 parts per million. As there is usually an ample concentration of unsaturated hydrocarbons to react with all the nitric oxide present it is the concentration of this constituent which determines the quantity of gum formed. Experience indicates that concentrations in excess of 0·05 part per million of nitric oxide may cause gum formation and subsequent trouble in the distribution system. Concentration of gum up to 20 parts per million does not appear to result in serious obstruction of appliances, but over 100 parts per million serious blockage may definitely be anticipated.

The formation of gum may be prevented by the removal of the nitric oxide, or alternatively the gum itself may be removed from the gas before distribution. The iron oxide purifiers normally absorb about half the nitric oxide and special methods of working the oxide purifying plant have been proposed whereby practically the whole of the nitric oxide can be removed. Catalytic oxidation of the nitric oxide and subsequent absorption has also been proposed.

The formation of the gum is a relatively slow reaction and the majority of it appears to be formed in the gas holders where there is sufficient time for the reactions to progress to completion. The newly formed gum appears as suspended particles of viscous liquid, the size of the drops varying from beyond the limit of the ultramicroscope to about 1·2 μ, these larger sizes constituting the majority of the gum formed. These particles settle fairly rapidly and the rate of deposition is accelerated if there is simultaneous condensation of water vapour. To this end live steam is sometimes introduced into the storage holders. The fact that many works are free from gum deposition although the crude gas contains appreciable quantities of nitric oxide suggests that conditions are suitable for the deposition of gum in the holders. The detection and estimation of the very

small concentrations of nitric oxide and suspended gum particles has necessitated the adoption of special methods of analysis. In this country the analytical methods employed have been developed largely by H. Hollings and his collaborators.

Estimation of Nitric Oxide. The following method is described by H. Hollings [1] and may be regarded as an adaption of the method originally proposed by Guyer and Weber.[2]

The gas is aspirated through a sintered glass washer and a spiral washer containing respectively Griess reagent and acid permanganate and then through ordinary washing bottles, one containing 15 per cent. sulphuric acid and the other ammoniacal zinc sulphate solution. Constant pressure and suction bottles at the beginning and end of the train respectively constitute a convenient means of controlling the gas flow which may be measured by a suitable meter.

Reagents.—The reagents are made up as follows :—

(*a*) Distilled water free from oxides of nitrogen (see below).
(*b*) A solution of 25 per cent. sulphuric acid. Dilute 27 ml. of conc. sulphuric acid with 180 ml. of water.
(*c*) A solution of potassium permanganate, 2·77 g. in 100 ml. of solution.
(*d*) A solution of acid permanganate. This should not be stored, but should be prepared as required by mixing 1 part by volume of (*b*) with 9 parts by volume with (*c*).
(*e*) A solution of sulphanilic acid. 600 ml. of (*a*) are boiled and 4 g. of sulphanilic acid added. This is then cooled and 200 ml. of glacial acetic acid are added and the solution is made up to 1 litre with (*a*).
(*f*) A solution of alpha-naphthylamine. 2·52 g. of the material are dissolved in cold glacial acetic acid and made up to 1 litre with (*a*). The solution is kept in a coloured bottle in the dark.
(*g*) A solution of Griess reagent. 1 part by volume of (*e*) is mixed with 1 part by volume of (*f*) and the mixture is diluted to 10 parts by volume with (*a*). This solution may be kept for several days, but for accurate work should be made up each day.
(*h*) A solution of sodium nitrite (Analar) containing 0·027 g. per litre for wet gas at 60° F. and 30 in. pressure or 0·029 g. per litre for dry gas at 0° C. and 760 mm. pressure. If well stoppered this solution will not change greatly during the course of a month.
(*j*) An *N*/5 solution of ammoniacal zinc sulphate.
(*k*) A 10 per cent. solution of sulphuric acid. Solutions (*j*) and (*k*) are not required when purified gas is being tested.

Method. The spiral washer is charged with 200 ml. of solution (*d*). The sintered glass washer is charged with 70 ml. of solution (*g*). The same volume of solution (*g*) is also placed in a stoppered Nessler glass to serve as a control solution. Gas is then passed through the acid permanganate solution into the Griess solution at a rate between 0·8 and 1·2 cu. ft. per hour. It is recommended that the gas should

1 H. Hollings, *Institution of Gas Engineers*, Comm. No. 147 (1936).
2 *Brennstoff-Chem.*, 1933, 14, 405.

be passed through solution (*d*) for a minute before coupling the washer to that containing the Griess reagent. This serves to displace air and to expel traces of oxides of nitrogen which may be introduced with the sulphuric acid.

Sufficient gas should be passed to produce a definite pink coloration in the Griess reagent. The acid permanganate reacts with the constituents of the gas other than nitric oxide and it is important that it should not become completely decolorised during a test. In general, one charge will last for an hour.

The Griess solution is then transferred completely to a Nessler glass provided with a stopper, and both it and the control are diluted to 100 ml. with (*a*). Solution (*h*) is added from a 1 ml. microburette to the control solution until the same depth of colour is produced as in the test solution; as the colour develops slowly, five minutes should elapse before each fresh addition and fifteen minutes before the final matching.

The strength of solution (*h*) is such that the addition of 1 ml. to the control indicates the presence of 1 p.p.m. of nitric oxide provided that 1 cubic foot of gas has been used in the test. This determination involves the assumption that one-third of the nitric oxide present is oxidised by the acid permanganate and reacts with the Griess reagent.

Crude gas should be washed before test to remove hydrogen sulphide and hydrogen cyanide, using solution (*j*) followed by solution (*k*). Purification with iron oxide should not be used. Purified gas containing more than 20 gr. of hydrogen cyanide must also be similarly treated before test. If a tar fog filter is used with crude gas, it must not be allowed to come into contact with air in the interval between tests.

It is important that contact of the Griess solution with the air should be reduced to a minimum; the effect of diffused light is unimportant. The Nessler tubes and the sintered glass washer should be kept scrupulously clean; glacial acetic acid is recommended for cleaning the washer. The acid permanganate washer should be rinsed after use, but should not be further cleaned more frequently than necessary, as the deposit formed improves its efficiency. When cleaning becomes necessary it is recommended that strong sulphuric acid or a sulphur dioxide solution be used. Hydrochloric acid must not be used.

Water Suitable for Use with the Griess Reagent. Water of satisfactory quality may be produced from a steam heated still operating in a room free from the products of combustion of gas. Where such water is not available the following method of treatment is recommended:—

An aqueous solution of iodine, prepared without addition of potassium iodide is added to the distilled water available, using

one-half of the amount which would produce a faint blue coloration in the presence of starch.

An apparatus based on the above method for the continuous estimation of nitric oxide has been described by H. Hollings in Communication No. 134 of the Institution of Gas Engineers (1937). The apparatus is now being made by Messrs Griffin & Tatlock Ltd.

Determination of Gum in Gas. Several methods are described by H. Hollings, and the simplest method consists in allowing a jet of gas to impinge on to a glass plate. For details of the apparatus employed (registered design No. 809014) see Communication No. 147 of the Institution of Gas Engineers, Appendix 2.

It has been found that the efficiency of gum removal is low at the start of a determination, if a plain cover-slip is used, but increases when there is a layer of gum on the glass. Cover-slips which are already gummed are therefore used, or alternatively, the cover-slip is given a gummy surface by placing on it a drop of saturated solution of gum in acetone. The solution must be quite syrupy, otherwise the gum will spread too far. The slip is placed in a steam oven to remove the solvent.

The slip is weighed before and after the test. If water is present the slip is dried in a vacuum desiccator. If oil is present the slip should be washed with light petroleum and then dried in a desiccator. It has been found by running parallel tests that the efficiency of gum removal depends to some extent upon the gas velocity.

Other methods described by the same author are the use of the ultramicroscope and thermal precipitation in which the gum is precipitated by passing the gas over an electrically heated wire between two glass plates. The gum collects on the plates in the form of a straight track. As the quantity is too small to weigh it has to be assessed by counting. A similar form of estimation is afforded by the Owens dust counter in which the gas is drawn at a high velocity through a slit, the gum or dust being deposited on a cover-plate placed behind the slit. The gum collects in a straight track, the size of which is matched against a standard plate. The instrument is stated to give reproducible results, but these are not always in agreement with those obtained by the use of the thermal precipitator.

B. Tar and Tar Products

The examination and analysis of tar products is treated separately on p. 87 *et seq.*

C. Ammonia Products

The treatment of gas liquor and the manufacture of sulphate of ammonia and other products therefrom is treated separately on p. 67 *et seq.*

D. Coke

Whereas coke manufactured in by-product coke ovens for use in blast furnaces, etc., is regarded as the primary product of this type of carbonizing plant, the coke produced by Gas Undertakings was, until recently, regarded as a residual product. Thus steps were taken to reduce the quantity of coke for sale by making water-gas and by steaming vertical retorts, etc. It is now appreciated that gas coke, when suitably prepared, is an excellent industrial and domestic fuel and considerable care is now exercised in its manufacture and subsequent treatment.

Coke, for whatever purpose, should be low in ash and moisture content. The proportion of ash is, of course, mainly determined by the quantity present in the original coal, although this is not uniformly distributed in the different sized pieces of coke. While the moisture content is initially a question of the quantity absorbed during the quenching and cooling of the coke, the subsequent exposure to atmospheric conditions will also influence this property.

The size of the coke is of primary importance. Gas coke is graded into a number of sizes, from material under ½ in. to ¾ in.—known as breeze—to pieces of over 3 in. in size. The relative proportions found in the different grades vary greatly with the origin of the coke, *i.e.* horizontal or vertical retorts, coke ovens, etc. When coke is sold for domestic and industrial uses, the following sizes are often adopted :—

Size	Grade
Up to ⅜ inch.	Coke breeze or dust.
⅜ ,, ¾ ,,	Coke nuts.
¾ ,, 1½ ,,	Domestic coke.
1½ ,, 2½ ,,	Medium coke.
Over 2½ ,,	Large coke.

To supply the demand for the smaller sizes for domestic boilers, etc., the large coke may be broken and re-graded. This process has the disadvantage that it produces a large quantity of breeze, the value of which is usually only about one-third of that of the larger sizes. It has already been noted that the ash is not uniformly distributed. The greater proportion of the ash is contained in the breeze, which may contain up to 20 per cent. In general, the larger the coke the lower is the ash. After breaking and screening large coke, the size ¾ in. to 1½ ins. may contain a higher ash content than the original coke. This is attributed to the fact that pieces of shale, etc., initially embedded in the larger coke are generally of the above size.

The moisture content of coke varies roughly in the same manner as the ash. By careful quenching it is possible to maintain a moisture content of 1 to 3 per cent., but it is possible for coke to contain up to 20 per cent.

Sampling. The same principles should be applied as in the sampling of coal (see p. 1).

Analysis.—For the determination of the moisture, ash, nitrogen and sulphur contents, the methods given on pp. 2 and 3 for coal should be used. Standardized methods of sampling and analysis have also been issued by the British Standards Institution, *B.S.* 496, 1933.

Phosphorus.—The phosphorus content is important in relation to the use of coke in blast furnaces. A variety of methods are employed for this determination, but the method adopted by the British Standards Institution (*B.S.* 735, 1937) may be taken as the simplest and most reliable. It is described on p. 3.

Volatile Matter.—The volatile matter left in coke gives a useful indication of the completeness of carbonization. The various methods

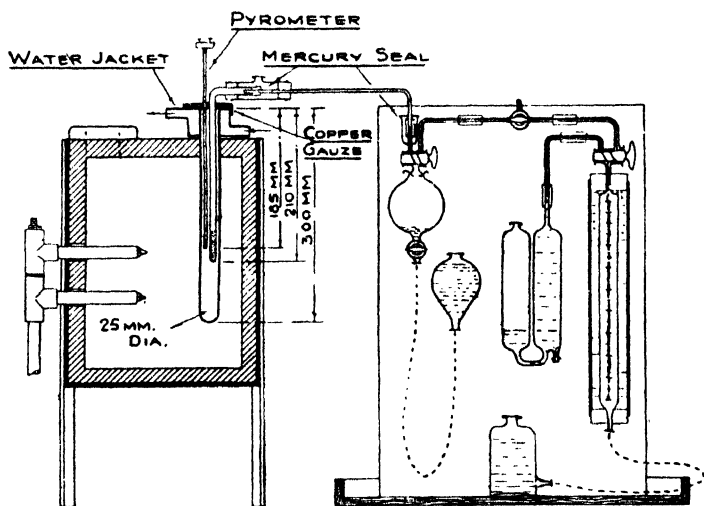



Fig. 14.

of determination given on p. 2 for coal may be employed. As the volatile content is usually only 1 to 3 per cent., a more accurate method has been devised by the South Metropolitan Gas Company [1] by which the volume and heating value of the residual gas may also be ascertained. This method is described below, and the apparatus used is shown in Fig. 14.

2 g. of the dried coke is placed in a silica tube which is itself placed inside a wider silica tube. In the outer tube is also placed a rare metal thermocouple so that the hot junction is opposite the coke sample. The silica tube is connected to a Hempel explosion pipette and to a measuring burette. After the apparatus has been connected up, the temperature is raised to 500° and the gas exhausted from the tube by the levelling bulb. The temperature is then increased to 1100° in nine to ten minutes, maintained for five minutes, and then lowered

[1] *Solid Products of the Carbonization of Coal*, London, 1934.

to 800°. All the gases evolved over this period are collected. The tube is then exhausted, and the gas thus obtained is added to that already collected. It is assumed that the gas is composed of carbon monoxide and hydrogen ; any carbon dioxide is removed by potash, and the residue mixed with the necessary air and exploded. The proportion of carbon monoxide and hydrogen can then be readily calculated (see Vol. I., p. 276). The test is to some extent empirical and does not indicate the whole of the volatile matter. Provided the test is carefully carried out, results agreeing within 0·1 therm per ton can be obtained. An average, well-carbonized horizontal coke contains volatile matter equivalent to about 1·2 therms per ton.

Physical Examination

The following physical properties of coke are examined in relation to its utilization as an industrial and domestic fuel :—

1. Hardness, resistance to abrasion, etc.
2. True and apparent specific gravity, and porosity.
3. Properties relating to its combustion.

1. **Strength of Coke.**—Considerable deterioration in the value of coke arises through the breakage caused on handling and the resulting production of breeze and dust. Oven coke is considerably stronger and harder than coke from horizontal and vertical retorts, the latter yielding probably the weakest material of these three methods of high temperature carbonization. As a test of the strength of coke, the shatter test is usually adopted in this country. This test is empirical and gives results which are only comparable when the procedure is standardized. The following test is specified by the British Standards Institution (see *B.S.* 496, 1933).[1]

(1) *Sample.* The sample consists of 250 lb. of coke over 2 in. in size taken as specified in *B.S.* 496 (1933).

(2) *Apparatus.* The shatter test apparatus consists of a box, 18 in. in width, 28 in. in length and approximately 15 in. in depth, supported above a rigidly mounted cast-iron or steel plate, not less than ½ in. in thickness, and not less than 38 in. in width and 48 in. in length. The inside of the bottom of the box, when in its highest position, is 6 ft. above the plate. The bottom of the box consists of two doors hinged lengthwise and latched so that they swing open freely and do not impede the fall of the coke. Boards about 8 in. in height are placed around the plate so that no coke is lost. To minimise the breakage of coke, which might otherwise occur while placing the sample in the box,

[1] Reprinted by permission from *British Standard Specification*, No. 496, 1933, " The Sampling and Analysis of Coke," official copies of which can be obtained from The British Standards Institution, 28 Victoria Street, London, S.W. 1.

the box is so suspended that it can be lowered to a convenient level for filling. The complete apparatus is shown in Fig. 15.

(3) *Description of Test.* 50 lbs. of the coke screened by hand over a 2 in. British Standard Coarse Mesh test sieve in such a way that any piece which can be passed through the screen in any position shall be counted as under size, is placed in the box of the shatter test apparatus. The coke is levelled, the box raised, and the coke dropped on to the

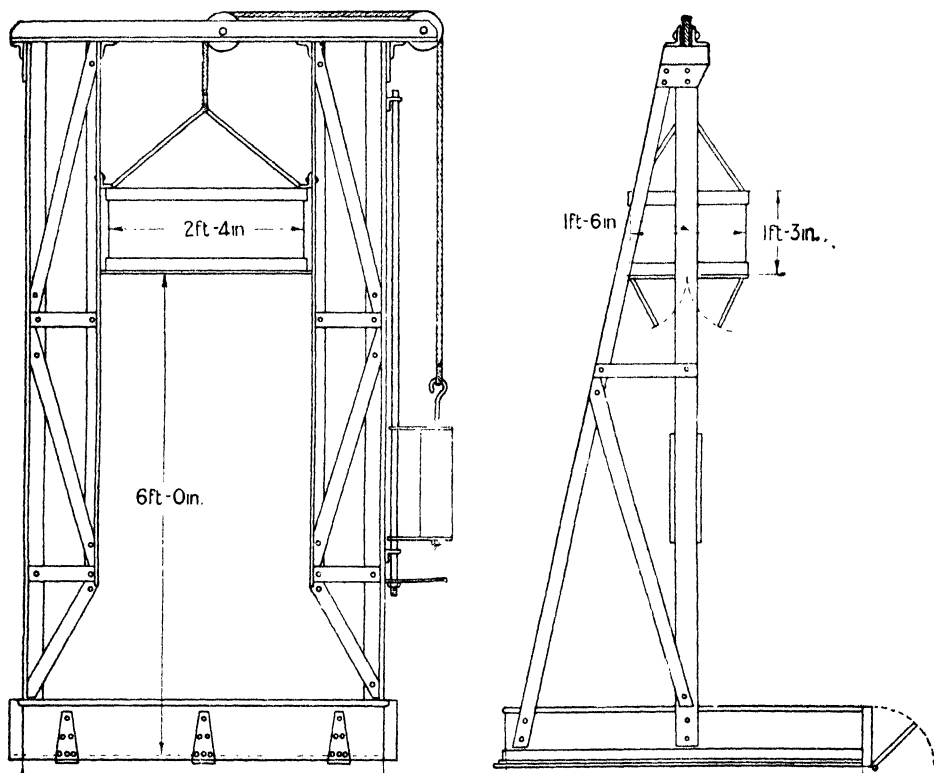



FIG. 15.

plate. The box is then lowered and all the coke shovelled into it indiscriminately, but taking care to avoid breakage. The box is again raised and the coke dropped again. When the coke has thus been dropped four times in all, it is screened by hand over 2 in., 1½ in., 1 in. and ½ in. British Standard Coarse Test sieves as described above, and the weights of coke of each grade determined to the nearest ounce.

(4) *Statement of Results.* At least three tests are made and the results recorded as percentages (given to 1 decimal place) remaining on the screens.

(5) *Shatter Index.* The shatter indices are the average of the

percentages retained on the respective screens. In general, the shatter indices reported are :—

1. The 2 in. index.
2. The 1½ in. index.

The shatter indices are given to the nearest whole number, except the ½ in. index which, when reported, is given to the first decimal place.

(6) *Tolerated Deviation.* If the average deviation of the individual results from their mean exceeds 2·5 and 1·5 units with the 2 in. and 1½ in. screens respectively, a further series of at least two tests are made, and the average of all the results taken.

Resistance to Abrasion.—To determine the resistance of coke to abrasion the trommel or barrel test may be used.

The test in principle consists in rotating a number of pieces of coke of a known size in a barrel or drum mounted on a horizontal axis, and subsequently determining the amount of breakage which has resulted. Different apparatus and procedure are employed in different countries, for details of which see Mott & Wheeler: *Coke for Blast Furnaces*, Iron and Steel Industrial Research Council, Technical Report No. 1, 1930. There is no universally adopted test in this country, but the following method has been employed by the Midland Coke Research Committee (see above reference). What may be termed the " Sheffield Coke Abrasion Test " is specified as follows :—In a drum 18 in. in diameter and 9 in. long, 1 cu. ft. of 3 to 2 in. coke is rotated during thirty minutes at 23 r.p.m. There is no objection to using a drum 18 in. in diameter and 18 in. long with a charge of 2 cu. ft. of coke. A sieving analysis is then made and the percentage of the charge remaining on a 1½ in. screen is noted. This figure is taken to be the " abrasion index."

2. (*a*) **Determination of Bulk Density.** (*B.S.* 496, 1933).—A cubical measure having a capacity of exactly 2 cu. ft. (5 in. on each internal edge) is used.

The coke from a shatter test (large, small and dust) is dropped into the measure from a shovel not more than 2 in. above it, until the coke is just level with the top, care being taken to prevent any undue voids, but without any shaking down.

The contents of the measure are then weighed. The weight, divided by two, gives the weight per cu. ft. of coke. The moisture content of the coke is also determined, and the bulk density expressed in terms of dry coke.

All determinations are made in duplicate, and further determinations are carried out, if the difference in duplicate results exceed 1 lb. per cu. ft.

(*b*) **Determination of True Specific Gravity.** — A suitable method for this determination is that of Greenwood & Cobb [1] which has now been standardized in *B.S.* 496, 1933.

A 50 ml. specific gravity bottle is cleaned with chromic acid, rinsed and filled with air-free distilled water, and then immersed in a bath of water at a convenient temperature (about 15°) during one hour. It is then weighed at this temperature (W_1 at t_1°). The bottle is then emptied, the neck dried, exactly 2 g. of dry coke, ground to pass a 72 mesh British Standard Test sieve, and 25 ml. of distilled water

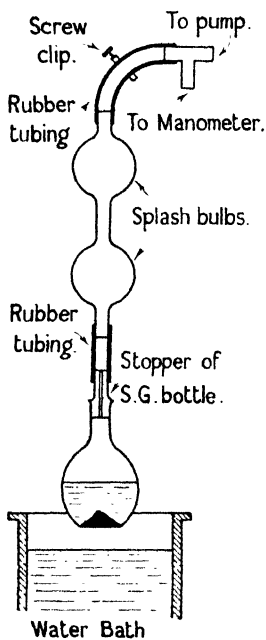
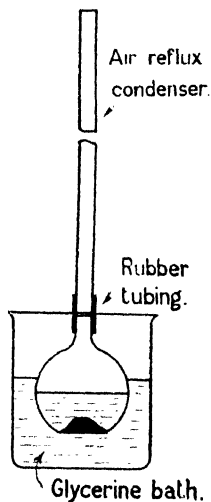



FIG. 16. FIG. 17.

are added. The entrained and occluded gas is removed by boiling under reduced pressure on a water bath, or under an air-reflux condenser on a glycerine-water bath, for half an hour.

While boiling under reduced pressure the stopper is inserted (to reduce the efflux of scum), using a splash bulb (see Figs. 16 and 17). After half an hour the clip is closed above the splash bulb, the suction stopped, and the clip re-opened to allow the water in the splash bulb to wash any scum into the bottle ; the bottle may be shaken to cause any scum to sink. If an air-reflux condenser is used, the scum is washed down with a few ml. of hot air-free distilled water.

[1] *J. Soc. Chem. Ind.*, 1922, **41**, 181 T.

The bottle is then allowed to stand for one hour in a bath of water at $t_2°$ (about 15°), then filled with air-free distilled water of the same temperature as the bath, and weighed (W_2).

If t_1 and t_2 are equal, the specific gravity

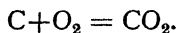
$$= \frac{W}{W + W_1 - W_2}.$$

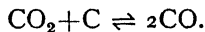
Where W = weight of dry coke (2·0 g.).

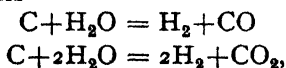
Precautions may be taken, for example, by using a thermostatically controlled bath, or by the use of cooling media, so that the bath temperatures t_1 and t_2 are the same, but if this cannot be conveniently ensured, a correction for the difference in temperature is made according to Fig. 18.

(*c*) **Apparent Specific Gravity.**—The British Standards Institution have not been able to recommend a reliable method for the determination of this property. The apparent specific gravity of the coke refers to the gravity of the coke plus all the pores contained therein. A method sometimes adopted is to cover a fragment of coke with paraffin wax. The liquid employed for the determination of the specific gravity by immersion is thereby prevented from displacing the air in the pores of the coke. For details of various methods which have been employed, see Mott and Wheeler, *Coke for Blast Furnaces*, Iron and Steel Industrial Research Council, Technical Report, No. 1, p. 67.

3. **Combustion of Coke.**—A large number of tests have been devised to obtain an indication or measure of the rate of combustion of coke in air, steam, etc. These are largely empirical, and attempts to compare results from different tests have led to considerable confusion. At low temperatures, the combustion of coke in air proceeds according to the reaction—

$$C + O_2 = CO_2.$$

This reaction takes place rapidly, and the carbon dioxide in passing through the upper layers of the heated coke, is reduced to carbon monoxide, viz. :—

$$CO_2 + C \rightleftharpoons 2CO.$$

This reaction takes place relatively slowly, the rate being dependent upon the temperature and the time of contact of the gases with the coke. The reaction is also influenced by the nature of the coke, and the rate of conversion of carbon dioxide to carbon monoxide for a given temperature and time of contact is taken as a measure of the reactivity of the coke. Similarly, the rate of decomposition of steam according to the reactions—

$$C + H_2O = H_2 + CO$$
$$C + 2H_2O = 2H_2 + CO_2,$$

may be used as a measure of reactivity. In the manufacture of water-gas, the reactivity of coke towards both carbon dioxide and steam

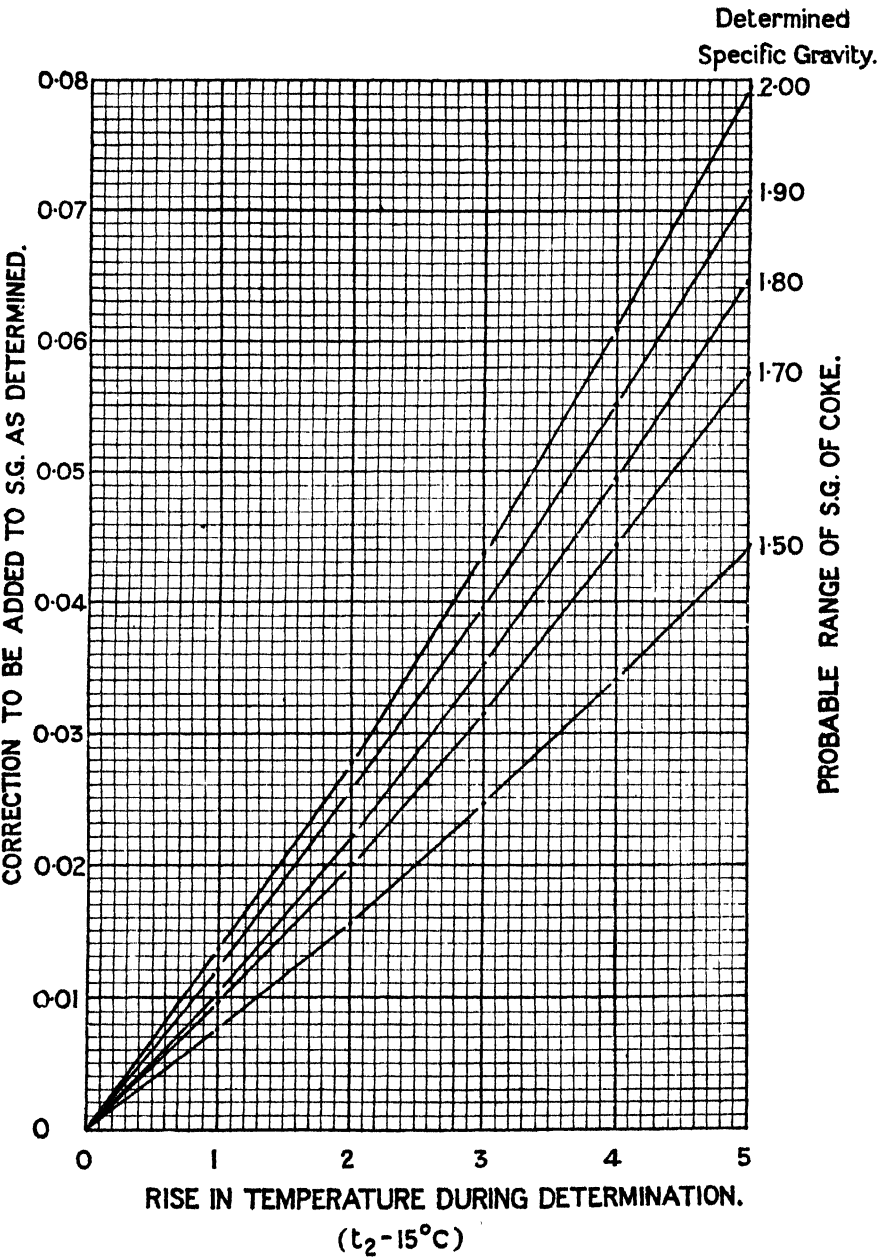



Fig. 18.

may appreciably influence the process, and numerous investigators have devised apparatus for the measurement of this property. The

results obtained vary considerably with the arrangement of the apparatus, temperature, time of contact, etc., and comparison between the results obtained by different methods is virtually impossible. The following method is employed by the Fuel Research Board :—

Carbon dioxide is passed over coke at 950° at a measured rate, and the proportion converted to carbon monoxide is determined. The number of c.c. of carbon monoxide formed per 100 c.c. of carbon dioxide is taken as the reactivity value. The reactivity does not remain constant for a given sample of coke, and hence the value initially obtained is termed reactivity " I," which corresponds to the initial reactivity value of the sample. Prolonged heating of the coke in nitrogen or *in vacuo* reduces the reactivity, and a second value is obtained, reactivity " II." Finally, after continued passage of carbon dioxide, the reactivity falls until a sensibly constant value, reactivity " III," is obtained. For details of the apparatus and the method of carrying out the test, see *Fuel Research Technical Paper*, No. 18 (1927). The following figures indicate the type of results which are obtained with different kinds of coke, using the above method :—

Coke.	Reactivity.		
	I.	II.	III.
Horizontal retort	145	131	78
Vertical retort	120	72	59
Yorks. By-Product	138	112	95
Blast furnace	43-98	40-72	33-60

When coke is burnt in a shallow fuel bed, little of the carbon dioxide is reduced to carbon monoxide, and the initial reaction, $C+O_2 = CO_2$, is the controlling factor. The above measurement of reactivity is not necessarily an indication of the rate of this reaction, and hence various tests have been devised to measure the rate of combustion under specific conditions. For details of such tests, reference should be made to *Coke for Blast Furnaces* (*loc. cit.*), and *The Solid Products of the Carbonization of Coal* (*loc. cit.*).

Ignition Temperature. The suitability of coke for domestic grates is to some extent dependent upon its ease of ignition. A measure of this property is obtained by the determination of the temperature of ignition. This is generally carried out by passing a current of air through a layer of coke, the temperature of which is slowly raised. The temperature of the coke is noted at frequent intervals, and the point at which it rises suddenly, due to the initiation of combustion in the coke, is taken as the ignition temperature. Obviously the method is largely empirical, and results are only comparable when obtained in the same type of apparatus. A convenient apparatus for this purpose is described in *The Solid Products of the Carbonization of Coal* (*loc. cit.*).

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AMMONIACAL LIQUOR AND AMMONIUM SALTS

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I. AMMONIACAL LIQUOR

THE aqueous condensates from the hydraulic main, foul main, and condensers, termed together "virgin liquor," and the ammoniacal liquor obtained by treatment of the gas with fresh water in the washers and scrubbers, are usually collected together in a common well or wells. The combined liquor contains practically the whole of the ammonia present in the crude gas, together with a considerable amount of sulphuretted hydrogen and carbon dioxide.

The liquor rarely, if ever, contains ammonia in the free state; it is usually present entirely as salts, of which the different sulphides and carbonates of ammonium constitute much the largest amount, while the chloride, thiocyanate, sulphate, thiosulphate, cyanide, and ferrocyanide are usually present in smaller quantity. The products primarily formed are the sulphides, carbonates, cyanide, and chloride, these being obtained from the sulphuretted hydrogen, carbon dioxide, hydrocyanic acid, and hydrochloric acid respectively contained in the crude gas; the other salts are formed from these by secondary reactions. The oxidation of the sulphides gives rise in the first instance to thiosulphate and polysulphide, but the latter immediately reacts with ammonium cyanide, forming the thiocyanate. The latter compound is also formed to a smaller extent by the combination of the ammonium sulphides with the carbon disulphide of the crude gas, to form ammonium thiocarbonate, which then undergoes conversion into thiocyanate. Ammonium cyanide, also, probably acts on the thiosulphates to some extent, forming ammonium thiocyanate and sulphite, and also attacks the iron of the apparatus slightly, forming ammonium ferrocyanide. The sulphites, and probably the thiosulphates, undergo slow oxidation to sulphate.

Polysulphide is rarely found in ammoniacal liquor owing to its reaction with the ammonium cyanide present, and the latter is also largely converted into thiocyanate in liquor which has been stored for some time. Linder has shown that free cyanide is frequently present even in stored gas-works liquor. Coke-oven liquors, which are usually not stored long enough for the production of polysulphide

by oxidation of the sulphide, often contain large amounts of cyanide, and on working up the liquor into ammonium sulphate, the waste gases may retain very considerable amounts of hydrocyanic acid, and become dangerous on account of the poisonous nature of this gas.[1]

In addition, the liquor always contains a considerable quantity of organic matter, of which the phenols form the largest proportion, and small amounts of nitrogenous bases such as pyridine and probably also amino-derivatives.

The ammonia present as sulphide, carbonate, and cyanide is distinguished as "volatile" ammonia, inasmuch as the ammonia present in this form is completely volatilized on boiling the liquid; the remainder is termed "fixed" ammonia, as it can only be driven off by the addition of a sufficient amount of a stronger alkali to combine with the whole of the remaining acid radicals present. In the combined gas-works liquor, some 75 to 80 per cent. of the ammonia is usually present in the "volatile" form, but in the virgin liquor the amount of "fixed" ammonia is much higher, amounting often to 75 per cent. of the whole.

Strength of Ammoniacal Liquor. In this country the strength is usually expressed by stating the number of ounces (by weight) of 100 per cent. sulphuric acid required to neutralize the ammonia present in 1 gallon of the liquor, this figure being known as the "oz. strength." Thus, for example, if a gallon of liquor requires 9·3 oz. of sulphuric acid per gallon, this would be known as 9·3 oz. liquor. For statistical purposes, such as expressing the yield of ammonia per ton of coal carbonized, or for the sale of liquor in bulk, it is customary to convert all quantities of such liquor into the equivalent volume of "10 oz. liquor."

1 gallon 10 oz. liquor contains 0·2169 lb. ammonia
= 0·8412 lb. ammonium sulphate.
Hence 10 oz. liquor is equivalent to 2·169 per cent. NH_3 *w/v*.

To obtain the parts of ammonia per 100 parts by weight of liquor it is necessary to divide the above percentage by the sp. gr., which is usually of the order of 1·02.

The above method of expressing the ammonia content of liquors has now no practical value, except that it is an accepted custom in the industries concerned and as such will probably continue to be employed.

Specific Gravity of Ammoniacal Liquor. As the ammonia is always present in the form of salts, the sp. gr. of the liquor is always greater than that of water, and contrary to solutions of pure ammonia, it increases with an increase in the ammonia content. For

[1] Cf. *Report on Alkali, etc., Works*, 1906, p. 33.

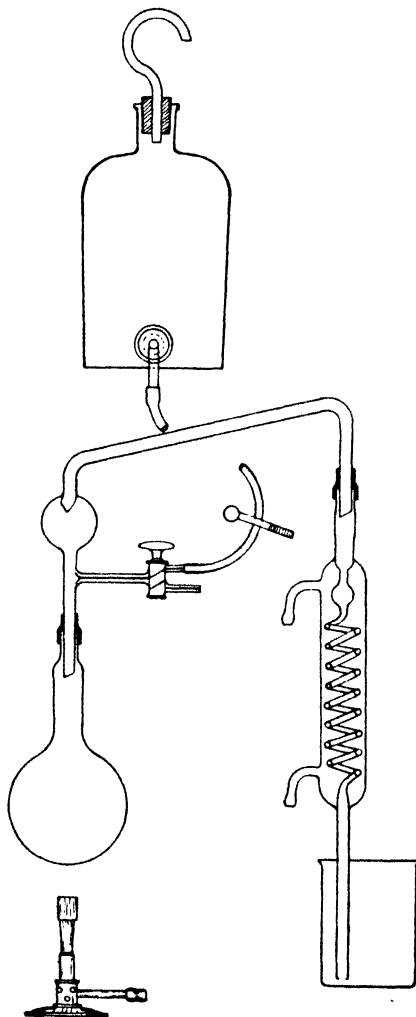
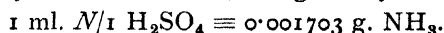
the purpose of the control of the working of the washers and scrubbers, the strength of the liquor is often inferred from its density as determined by Twaddell's hydrometer, it having been found that each degree Tw. corresponds approximately to 2 oz. strength of liquor, so that the oz. strength is found roughly by doubling the Twaddell hydrometer reading. Naturally, owing to the varying proportions of ammonium salts present, this estimate is only of a very approximate nature, and although sufficiently accurate for works control purposes, is quite inadmissible if any degree of accuracy is required. Thus, a liquor showing 5° Tw. and taken as 10 oz. strength may vary actually between 8 and 12 oz. in extreme cases, and in the case of virgin liquor especially, the strength inferred from the density is much too high.

FIG. 19.

A. ANALYSIS OF AMMONIACAL LIQUOR

1. **Total Ammonia.**—The method almost invariably employed consists in distilling off all the ammonia in the presence of an excess of fixed alkali, and collecting the distillate in a known volume of standard acid solution.

For the determination, 10 ml. to 25 ml. according to the strength of the liquor, is measured into the distillation flask shown in Fig. 19, diluted to about 200 ml. and the flask connected up to the condenser. The receiving vessel is charged with a known volume of $N/1$ sulphuric acid solution. 20 ml. of 5 per cent. sodium hydroxide solution is run into the distillation flask, and the liquor distilled until about 10 to 20 ml. of the solution remains in the flask. At the conclusion of the distillation, the distillate is titrated with $N/1$ sodium hydroxide solution, using methyl orange as indicator.

$$1 \text{ ml. } N/1 \ H_2SO_4 \equiv 0{\cdot}001703 \text{ g. } NH_3.$$

2. **Volatile Ammonia.**—For the separate determination of the volatile ammonia, the analysis is carried out in exactly the same manner as above, with the omission of the addition of sodium hydroxide solution to the liquor before distillation.

Direct determination of the volatile ammonia by titrating the liquor with sulphuric acid solution, using methyl orange as indicator, does not give satisfactory results, the end-point of the reaction being very uncertain.

3. **Fixed Ammonia.**—This may be determined by the addition of sodium hydroxide solution to the residue in the distillation flask after the determination of the volatile ammonia and then distilling as before, or by deducting the amount of volatile ammonia from the total ammonia.

B. Complete Analysis

The analysis of the remaining constituents of the ammoniacal liquor is not required in the ordinary gas-works routine, but is of use for special purposes.

The estimation of total, volatile and free ammonia is carried out as described above; the methods for the remaining constituents are as follows:—

1. **Carbonic Acid.**—10 ml. of the liquor (or more if dilute) is diluted to 400 ml. in a flask fitted with a Bunsen rubber valve, 10 ml. of ammoniacal calcium chloride solution (1 ml. = 0·044 g. CO_2) added, and the whole heated on a water-bath for one and a half to two hours. The precipitated calcium carbonate is filtered off, washed, the precipitate washed back into the flask, dissolved in a known volume of *N*/2 hydrochloric acid, and the excess of acid titrated back with *N*/2 sodium carbonate, using methyl orange as indicator. The small amount of calcium carbonate remaining on the filter is best recovered by incineration, the ash being placed in the flask before adding the acid.

1 ml. *N*/2 hydrochloric acid ≡ 0·011 g. CO_2.

When analyzing concentrated ammonia liquor, 25 ml. is diluted to 250 ml. in a standard measuring flask. 10 ml. of this dilute solution (= 1 ml. original liquor) is taken for carbonic acid estimation.[1]

2. **Hydrochloric Acid.**—10 ml. of the liquor is diluted to 150 ml. boiled to remove volatile ammonia, and then boiled for a further fifteen minutes with addition of 25 ml. of hydrogen peroxide (10 vols.). Five or six drops of 10 per cent. potassium chromate solution are then added, and the whole boiled for two minutes, after which a slight excess of sodium carbonate is added and the boiling continued for one minute. The filtered and cooled solution is made up to 250 ml.

[1] See also Astley and Greenwood, *J. Soc. Chem. Ind.*, 1939, **58**, 251.

and an aliquot portion titrated with neutral $N/10$ silver nitrate, after neutralization with dilute nitric acid.

1 ml. $N/10$ $AgNO_3$ solution $\equiv$ 0·003647 g. HCl.

A blank experiment should be made with 10 ml. of $N/10$ sodium chloride solution and the same volumes of water, peroxide, chromate and carbonate, to determine the correction for traces of chloride in the reagents used. Sometimes the organic matter resists oxidation, in which case more hydrogen peroxide must be added, and the boiling continued for a longer period.

3. **Sulphuric Acid.**—250 ml. of the liquor is concentrated to about 10 ml., 2 ml. of concentrated hydrochloric acid added, and the evaporation continued to decompose the thiosulphate and render the organic matter less soluble. The residue is extracted with water, filtered, and made up to 250 ml., of which 100 ml. is treated with 10 per cent. barium chloride solution. The precipitated barium sulphate is filtered off, washed, ignited, and weighed.

Grams H_2SO_4 per 100 ml. = $BaSO_4 \times 0{\cdot}4202$.
Grams S as H_2SO_4 per 100 ml. = $BaSO_4 \times 0{\cdot}1374$.

4. **Hydrogen Sulphide.**—According to Linder,[1] 10 ml. of the liquor (or more if dilute) is added to an excess of an ammoniacal zinc chloride solution, diluted to about 80 ml. with warm water, and the solution heated to about 40° in order to coagulate the zinc sulphide, which is then filtered and washed with water at 40° to 50°. The filter paper containing the zinc sulphide is placed in an excess of $N/10$ iodine solution mixed with hydrochloric acid. After vigorous shaking to effect complete solution of the zinc sulphide, the excess of iodine is determined by titration with $N/10$ sodium thiosulphate, using starch solution as indicator.

1 ml. $N/10$ iodine solution $\equiv$ 0·0017 g. H_2S.
1 ml. $N/10$ iodine solution $\equiv$ 0·0016 g. S.

Mayer and Hempel [2] prefer to employ a cold solution of ammoniacal zinc acetate for precipitation of the zinc sulphide, and to wash with cold water containing ammonium salts, but otherwise they proceed in the same manner as Linder.

5. **Sulphite and Thiosulphate.**—Linder [3] found that only in exceptional cases is it possible, by the use of iodine, to determine these constituents in liquor. A united figure for these two constituents may be obtained by difference by subtracting the amount of sulphur present as sulphate, thiocyanate and sulphide from the total sulphur content.

[1] *Reports on Alkali, etc., Works*, 1902, p. 71; 1903, p. 31; 1904, p. 27; 1905, p. 26; 1906, p. 33; 1907, p. 53; 1908, p. 17; 1909, p. 15.

[2] *J. Gasbeleucht.*, 1908, **51**, 381.

[3] *Loc. cit.*

Mayer and Hempel[1] have suggested the determination of the following data as an approximate method. The total quantity of iodine taken up by the original liquor is first ascertained, the number of ml. being denoted by A. To obtain a definite end-point in the reaction, the acidified liquor must not be titrated directly with iodine, but an excess must be added and the excess of iodine titrated back with thiosulphate and starch. In another equal volume, the hydrogen sulphide is determined by the method given above, the number of ml. of iodine required being denoted by B. A further equal volume is then mixed with an ammoniacal solution of zinc and strontium chlorides, the former removing the sulphide and the latter the sulphite. The filtrate contains the thiosulphate, and is titrated with iodine as before, the number of ml. of iodine required being denoted by C. The following data are thus obtained in terms of the iodine solution :—

Sulphide = B
Thiosulphate = C
Sulphite = $A-(B+C)$.

The figures for sulphite and especially for thiosulphate are probably only very approximate, owing to the fact that the organic matter present in the liquor materially affects the quantity of iodine used both in the titration of the original liquor, and in that of the liquor after removal of the sulphide and sulphite.

6. **Total Sulphur.**—50 ml. of liquor (100 ml. if dilute) is slowly dropped into a flask containing an excess of bromine free from sulphur, covered with water and moderately acidified with hydrochloric acid, the flask being constantly shaken during the addition. The oxidized solution is evaporated to dryness on the water-bath, the residue extracted with water, made up to 250 ml., and 100 ml. precipitated with a 10 per cent. barium chloride solution as barium sulphate, which is filtered off, dried, ignited, and weighed.

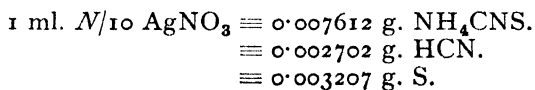
$$\text{Grams sulphur} = 0{\cdot}1374 \times \text{g. } BaSO_4.$$

Certain liquors, especially from coke ovens and blast furnaces, yield a heavy precipitate of brominated phenols, which retain traces of sulphate. This is recovered by fusing the residue insoluble in water with as small a quantity as possible of potassium carbonate and nitrate, or of sodium peroxide, and subsequent precipitation with barium chloride solution.

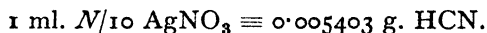
7. **Thiocyanate.**[2]—(1) *Ferrocyanide Absent.* 50 ml. of the liquor is treated with lead carbonate to remove sulphide, and the lead

[1] *Loc. cit.*
[2] For general methods of determination of Cyanogen Compounds, *cf.* Vol. I., p. 621 *et seq.*

sulphide, together with the excess of lead carbonate, filtered off and washed. The filtrate and washings are treated with sodium sulphite containing sulphurous acid, so that it is just acid, warmed, an excess of 10 per cent. copper sulphate solution added, and the whole digested at 70° to 80° for five to ten minutes. The precipitated cuprous thiocyanate is filtered off and washed free from copper solution. The filter paper and precipitate are then transferred to the beaker or flask used for the precipitation, and digested at 30° to 40° with 25 ml. of a 4 per cent. sodium hydroxide solution free from chloride. After filtering off and washing the cuprous hydroxide formed, the cold filtrate is acidified with dilute nitric acid free from oxides of nitrogen, filtered if necessary, and titrated with $N/10$ silver nitrate, using iron alum as indicator.

$$1 \text{ ml. } N/10\ AgNO_3 \equiv 0{\cdot}007612 \text{ g. } NH_4CNS.$$
$$\equiv 0{\cdot}002702 \text{ g. } HCN.$$
$$\equiv 0{\cdot}003207 \text{ g. } S.$$

(2) *Ferrocyanide Present.* 50 ml. of liquor is made just acid with sulphuric acid, ferric alum solution added until the solution is strongly coloured by ferric thiocyanate, and the solution warmed to 60°. It is then filtered through a folded filter paper, and the precipitate of Prussian blue washed with water containing sodium or ammonium sulphate; the filtrate is then treated as above.

8. **Total Hydrocyanic Acid.**—For this estimation Feld's[1] method is employed. 50 ml. of the liquor is diluted to about 150 ml. in a large flask, a solution of about 5 g. of lead nitrate added, and the whole distilled for twenty to thirty minutes. The steam evolved is condensed and collected in 25 ml. of $N/1$ sodium hydroxide in a receiver, the end of the condenser dipping below the surface of the liquid. The cyanogen present in the form of cyanides distils over as hydrocyanic acid and is converted into sodium cyanide in the receiver. The amount is estimated by diluting the distillate to 400 ml. adding a crystal of potassium iodide, and titrating with $N/10$ silver nitrate solution until a permanent precipitate of silver iodide is formed.

$$1 \text{ ml. } N/10\ AgNO_3 \equiv 0{\cdot}005403 \text{ g. } HCN.$$

In some cases the liquid froths up considerably during distillation, and it is therefore advisable to use a flask of large capacity and to heat cautiously at first.

9. **Ferrocyanic Acid.**—250 ml. of the liquor is treated with lead carbonate to remove sulphide, and the residue filtered off and washed. The filtrate and washings are then acidified with 10 per cent. sulphuric acid solution, ferric alum solution added until the

[1] *J. Gasbeleucht.*, 1903, 47, 565.

solution is strongly coloured by ferric thiocyanate, and the whole warmed to 60°. The solution is filtered to remove the precipitated Prussian blue, this being washed with water containing sodium sulphate. The filter paper and precipitate are then transferred to a beaker and boiled for five minutes with 25 ml. of a 5 per cent. potassium hydroxide solution and allowed to cool. When cool the solution is filtered. The filtrate is then transferred to a flask and acidified with 10 per cent. sulphuric acid, and 0·2 to 0·3 g. cuprous chloride added. It is then distilled, and the distillate collected in 25 ml. of *N*/1 sodium hydroxide, this being titrated with *N*/10 silver nitrate solution using potassium iodide as indicator.

$$1 \text{ ml.} \equiv 0{\cdot}00947 \text{ g. } (NH_4)_4Fe(CN)_6.$$

10. **Pyridine.**—The method described below is based upon the complete oxidation of free ammonia by boiling sodium hypobromite solution, pyridine being unaffected.[1]

100 ml. of the sample is measured into a litre flask fitted with a bung and a right-angled bend. A few drops of methyl orange indicator are added and the liquor rendered just acid with dilute sulphuric acid solution. The solution is then boiled to drive off carbon dioxide and hydrogen sulphide, and cooled. *N*/10 sodium hydroxide solution is added until the solution is almost neutral, the final neutrality being obtained by the use of *N*/1 sodium hydroxide, an excess of 7 ml. being subsequently added. The above flask is now connected to a second litre flask by means of a tube which passes to the bottom of the second flask. The outlet of the latter is fitted with a splash head and connected to a water-jacketed condenser, the outlet of which dips into a 500 ml. CO_2 flask. This second flask is charged with 150 ml. of sodium hypobromite solution, prepared by dissolving 100 g. of sodium hydroxide in 1 litre of water, and agitating with 25 ml. of bromine. 20 ml. of *N*/10 sulphuric acid solution is placed in the receiver, the apparatus connected up, and the sample distilled vigorously for twenty to thirty minutes. The sodium hypobromite solution is warmed prior to the commencement of the distillation, and should be kept at boiling point for at least ten minutes when the distillation is nearing completion, so as to ensure expulsion of any pyridine condensed in the initial stages. To the distillate are added several drops of phenolphthalein indicator and one or two drops of methyl orange. Titration is carried out with *N*/10 sodium hydroxide solution (free from carbonate), the burette reading being taken at both the methyl orange (*a* ml.) and phenolphthalein end-points (*b* ml.). The methyl orange titration (*a*) represents the excess acid present, and the total sodium hydroxide (*b*) represents this plus the

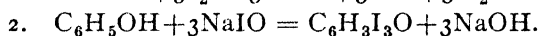
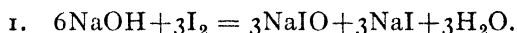
[1] *American Gas Chemists' Handbook*, 1922, p. 235.

acid combined with pyridine. Then 0·08 $(b-a)$ = g. pyridine per litre of gas liquor.

11. **Phenols.**—For the estimation of the amount of phenols in ammoniacal liquor, the most suitable method is that of Skirrow,[1] which depends upon the isolation of these compounds by distillation of the acidified liquor with steam, and treatment of the distillate with an excess of standard iodine solution, titrating back with sodium thiosulphate solution according to the method of Messinger and Vortmann.[2]

The treatment with iodine takes place in alkaline solution, the reactions being as follows :—

$$1.\quad 6NaOH+3I_2 = 3NaIO+3NaI+3H_2O.$$

$$2.\quad C_6H_5OH+3NaIO = C_6H_3I_3O+3NaOH.$$

Each molecule of phenol (or its homologues), therefore, effects the conversion of six atoms of iodine into tri-iodophenol and sodium iodide, and the excess above this proportion forms a mixture of sodium hypoiodite and iodine with the alkali, which on the addition of acid is converted into free iodine and may be estimated with sodium thiosulphate :—

$$NaIO+NaI+H_2SO_4 = I_2+Na_2SO_4+H_2O.$$

To carry out the estimation,[3] 100 ml. of the liquor is treated with ammonium polysulphide solution, diluted after standing to 200 ml., and the hydrogen sulphide removed by treatment with lead carbonate. The solution is filtered, to the filtrate is added 25 ml. of a 50 per cent. solution of sodium hydroxide, and the solution evaporated on a water-bath until separation of salts takes place. The residual liquor and salts are washed into a distilling flask, made slightly acid with 30 per cent. sulphuric acid solution, and treated with a little lead carbonate and 1·5 to 2 g. of precipitated chalk. The whole is well mixed, 25 g. of sodium chloride added, and the solution distilled through a Liebig condenser until approximately 250 ml. of the distillate is obtained. Water is added to the distilling flask through a drop funnel in order to maintain the liquid level approximately constant throughout the whole period of distillation. Titration of the phenols proceeds as follows :—

A preliminary titration is carried out with 10 ml. of the distillate, using a large excess of $N/2$ sodium hydroxide (about 1 ml.) in order to determine approximately the amount of phenol present. A volume of the distillate, equivalent to about 8 ml. of $N/10$ iodine solution, is then diluted to 100 ml. in a stoppered flask, and the correct volume

[1] *J. Soc. Chem. Ind.*, 1908, **27**, 58.

[2] *Ber.*, 1889, **22**, 2313. *Cf.* also Korn, *Z. anal. Chem.*, 1906, **45**, 552.

[3] *Report on Alkali, etc., Works*, 1927, p. 19.

of $N/2$ sodium hydroxide solution added (0·133 ml. $N/2$ sodium hydroxide for each ml. of $N/10$ iodine solution reduced). The solution is then heated to 60°, 10 ml. of $N/10$ iodine solution added slowly with agitation, the solution cooled, and then acidified with $N/2$ sulphuric acid solution. Titration is carried out finally against $N/10$ sodium thiosulphate solution, using starch indicator, the end-point of the reaction being indicated by a transition of colour from blue to rose pink.

$$1 \text{ ml. } N/10 \text{ iodine} \equiv 0{\cdot}001567 \text{ g. } C_6H_5OH.$$

The phenols present are all calculated as phenol, C_6H_5OH, but actually some 35 per cent. of the whole consists of higher homologues, chiefly cresols; as the latter combine with a smaller proportion of iodine than phenol, the results obtained are rather low.

For a rapid approximate estimation of the phenols in ammoniacal liquor, White and Clary [1] acidify 1 litre of the liquor with concentrated hydrochloric acid, extract with 100 ml. of chloroform by shaking in a separating funnel, and evaporate the chloroform extract in a flask. The weight of residual phenols amounts approximately, under these conditions, to one-quarter of the total amount present.

12. **Polyhydric Phenols.**—A rough estimation of the quantity of polyhydric phenols is obtained by the following tests,[2] the results of which can be given in terms of oxygen absorbed or alternatively as catechol.

(a) *Burette Aeration Test.* For this determination a Bunte burette is required, with graduations carried down 10 ml. below the zero point, and allowing about 7 ml. of free space above the lower stopcock. The capacity of the tubulus below the stopcock should be 1 ml., and the total capacity of the burette and tubulus, 118 ml.

To carry out the test, 19 ml. of the liquor is drawn into the burette through the lower tubulus, leaving this charged with the liquor—20 ml. in all. The burette is then placed with its tubulus in a small cup containing about 10 ml. of a 10 per cent. sodium hydroxide solution, and suction is again applied until the upper level of the liquid stands at approximately the +9 ml. mark. The burette is now placed in a water cylinder with the upper stopcock open, and allowed to stand until the temperature conditions are constant. The upper stopcock is then closed, about 1 ml. of distilled water run into the cup, the cock opened, and the water allowed to enter the burette until the pressure conditions are again constant. The air in the burette is thus measured under slight excess pressure equivalent to about 2 mm. of mercury—a negligible amount.

The contents of the burette are now shaken for five minutes, the

[1] *J. Gas Lighting*, 1905, **92**, 467.

[2] *Report on Alkali, etc., Works*, 1927, p. 20.

burette returned to the water cylinder, and pressure conditions adjusted as before by the admission of distilled water. This procedure is repeated until the volume of water required to raise the pressure does not exceed 0·2 to 0·3 ml., at which point absorption can be taken to be complete. The brown residual liquid is finally displaced by water in the usual manner, and the residual volume of gas read off at approximately the same temperature and pressure as before. The oxygen absorbed in parts per 100,000 = P = ml. oxygen used (0° C., 760 mm.)$\times 5 \times 1{\cdot}43$, and polyhydric phenols in terms of catechol $= P \times 1{\cdot}88$.

(b) *Colour-Producing Bodies.* Polyhydric phenols are considered to be responsible for the greater part of the objectionable brown colour acquired by spent liquors on exposure to air, but the possibility that other oxygen-absorbing bodies are present cannot be excluded. In making the determination, 10 ml. of the liquor is diluted to 100 ml. An aliquot portion of this solution is diluted to 80 ml., 5 ml. of a 2*N* ammonia solution added, the volume made up to 100 ml., and the solution shaken in a wide glass-stoppered bottle before transference to a 100 ml. Nessler glass. A standard colour solution is now prepared under the same conditions, by means of a freshly prepared solution of catechol (1 ml. = 0·0011 g. $C_6H_4(OH)_2$). This is added to a test solution containing the same amounts of ammonia, thiocyanate and thiosulphate as the liquor, diluted to 100 ml., and shaken with air in the manner described. About 0·5 to 1 ml. of the catechol solution is a convenient volume to employ, and the solutions should be allowed to stand five to ten minutes before the final comparison of the colour tints.

1 ml. of catechol solution = 0·0011 g. $C_6H_4(OH)_2$.

13. **Oxygen-Absorption Value.**—There are present, in both crude and still effluent liquors, various compounds which are capable of absorbing oxygen, *i.e.* sulphide, thiosulphate, thiocyanate, monohydric and polyhydric phenols. The bulk of the oxygen is absorbed by the phenols, particularly with liquors from vertical retorts and low temperature carbonization processes, where the tar with which the liquor is in contact contains a considerable proportion of these compounds. Such liquors absorb oxygen freely, and acquire a deep brown tint, a property which is characteristic of catechol, hydroquinone, pyrogallol and other homologues. The estimation of these bodies is of importance in relation to the quantity of oxygen which they can absorb. Effluent liquor from sulphate stills is frequently disposed of *via* sewage treatment systems, and the quantity which can be dealt with is determined by the amount of oxygen which is absorbed from the bacteria filters, etc., of the sewage plant. It is obviously desirable that this figure should be as low as possible in order that

the purification process may be worked, and to this end it is necessary to know which constituents of the liquor are liable to oxidation, and to what extent. A measure of the total oxygen absorbed is shown by the volume of potassium permanganate which is reduced, and hence decolorised, by the liquor. Since oxygen is freely absorbed by these liquors on exposure to air, the sample should be kept out of contact with air until the test is to be carried out.

Permanganate Test for Oxygen-Absorption Value. In the case of effluent liquor, 1 ml. is suitable for this determination. When analyzing concentrated liquor or gas liquor, however, a 5 per cent. solution should be prepared, and 1 ml. of this solution taken for analysis.

20 ml. of distilled water is placed in a 250 ml. glass-stoppered bottle, 10 ml. of 10 per cent. sulphuric acid solution added, and *N*/80 potassium permanganate solution run in from a burette until a faint permanent colour is obtained in the solution. 50 ml. of *N*/80 potassium permanganate solution is then added from a burette, followed by the required volume of the liquor to be analysed. The bottle is then tightly stoppered and immersed in a water-bath at 27° for four hours, with periodical agitation. At the completion of the time period a crystal of potassium iodide is added, and the quantity of iodine released is determined by titration with *N*/80 sodium thiosulphate solution, using starch solution as indicator. The result is expressed as parts of oxygen absorbed per 100,000 parts of liquor.

1 ml. *N*/80 $KMnO_4$ solution = 0·0001 g. oxygen.

An approximate oxygen-absorption value of a liquor can be obtained using the same procedure, but limiting the period of the test to three minutes.

The results obtained by the four hours' test may be compared with the oxygen absorption values of the known constituents of the liquor, these values being calculated from the analysis of the liquor. The

	Parts per 100.	Equivalent oxygen-absorption (parts per 100,000).
Monohydric phenols (as C_6H_5OH)	0·230	410
Thiocyanate (as CNS)	0·045	40
Thiosulphate (as S)	0·023	20
Colour-producing bodies (as catechol)	0·550	470
Oxygen absorbed in 4 hours' permanganate test	...	885
Oxygen absorbed in burette test	...	115
Oxygen absorbed by other bodies (by difference)	...	415

foregoing example[1] illustrates the correlation between the oxygen-absorption values of the constituents of a liquor and the total value as determined by the permanganate test.

If catechol alone were present, the burette figure would be equal to $0{\cdot}115 \times 1{\cdot}88 = 0{\cdot}22$ part of catechol per 100 parts liquor. As the liquor has been partially oxidized, the figure given by the colour test is considerably higher.

C. Concentrated Gas Liquor

It is now the practice at many works to concentrate the crude gas liquor up to a strength of 15 to 20 per cent. ammonia, at which strength it may be sent to adjacent chemical works at a greatly reduced transport cost. The concentrated liquor contains only the volatile impurities originally present in the weak liquor. The fixed ammonia is not recovered, but allowed to go to waste in the effluent liquor. For the analysis of concentrated gas liquor, the methods given above may be employed, with suitable modification in the quantity of liquid taken in view of the increased concentration. In the estimation of hydrogen sulphide, special care should be taken to reduce the oxidation of the precipitate, which takes place rapidly and gives rise to low results.

D. Liquor Ammonia

I. Manufacture

In the manufacture of pure ammonia solutions from gas liquor the various acid and basic constituents must be removed. By heating the liquor to about 100°, some 80 to 90 per cent. of the carbon dioxide and hydrogen sulphide are evolved, together with ammonia equivalent to its partial pressure at that temperature. This ammonia can be removed by washing the gases with liquor or water, or by passing them through the saturator of a sulphate plant, the ammonia being absorbed by the acid, and the acid gases passing forward. To remove the remaining acid gases, the liquor is distilled after admixture with lime. It is impossible in this way to free the ammonia completely from carbon dioxide, hydrogen sulphide, etc., and it is therefore the practice first to dephlegmate the gases to remove the water, and then pass them through suitable purifying solutions. For the acid gases, lime or soda solutions are employed, while to remove pyridine and other organic impurities the gases are passed through active carbon filters, or scrubbed with heavy tar or mineral oils.

[1] *Report on Alkali, etc., Works,* 1927, p. 22.

II. Analysis

1. **Strength of Solution.**—This is usually estimated from the sp. gr. by the table given below, but may also be determined by titration with standard acid. The strongest ammonia solution sold commercially has a sp. gr. of about 0·880, contains 36 per cent. of ammonia, and is sold as "0·880" ammonia.

Specific Gravities of Ammonia Solutions at 15° C.*

Sp. gr. at 15° C.	Per cent. NH_3 (by weight).	g. NH_3 per litre.	Correction of the sp. gr. for ±1° C.	Sp. gr. at 15° C.	Per cent. NH_3 (by weight).	g. NH_3 per litre.	Correction of the sp. gr. for ±1° C.
1·000	0·00	0·0	0·00018	0·940	15·63	146·9	0·00039
0·998	0·45	4·5	0·00018	0·938	16·22	152·1	0·00040
0·996	0·91	9·1	0·00019	0·936	16·82	157·4	0·00041
0·994	1·37	13·6	0·00019	0·934	17·42	162·7	0·00041
0·992	1·84	18·2	0·00020	0·932	18·03	168·1	0·00042
0·990	2·31	22·9	0·00020	0·930	18·64	173·4	0·00042
0·988	2·80	27·7	0·00021	0·928	19·25	178·6	0·00043
0·986	3·30	32·5	0·00021	0·926	19·87	184·2	0·00044
0·984	3·80	37·4	0·00022	0·924	20·49	189·3	0·00045
0·982	4·30	42·2	0·00022	0·922	21·12	194·7	0·00046
0·980	4·80	47·0	0·00023	0·920	21·75	200·1	0·00047
0·978	5·30	51·8	0·00023	0·918	22·39	205·6	0·00048
0·976	5·80	56·6	0·00024	0·916	23·03	210·9	0·00049
0·974	6·30	61·4	0·00024	0·914	23·68	216·3	0·00050
0·972	6·80	66·1	0·00025	0·912	24·33	221·9	0·00051
0·970	7·31	70·9	0·00025	0·910	24·99	227·4	0·00052
0·968	7·82	75·7	0·00026	0·908	25·65	232·9	0·00053
0·966	8·33	80·5	0·00026	0·906	26·31	238·3	0·00054
0·964	8·84	85·2	0·00027	0·904	26·98	243·9	0·00055
0·962	9·35	89·9	0·00028	0·902	27·65	249·4	0·00056
0·960	9·91	95·1	0·00029	0·900	28·33	255·0	0·00057
0·958	10·47	100·3	0·00030	0·898	29·01	260·5	0·00058
0·956	11·03	105·4	0·00031	0·896	29·69	266·0	0·00059
0·954	11·60	110·7	0·00032	0·894	30·37	271·5	0·00060
0·952	12·17	115·9	0·00033	0·892	31·05	277·0	0·00060
0·950	12·74	121·0	0·00034	0·890	31·75	282·6	0·00061
0·948	13·31	126·2	0·00035	0·888	32·50	288·6	0·00062
0·946	13·88	131·3	0·00036	0·886	33·25	294·6	0·00063
0·944	14·46	136·5	0·00037	0·884	34·10	301·4	0·00064
0·942	15·04	141·7	0·00038	0·882	34·95	308·3	0·00065

* Lunge and Wiernik, *Z. angew. Chem.*, 1889, **2**, 181.

2. **Inorganic Impurities.**—Technically pure liquor ammonia should be clear and colourless, even on exposure to light. Sulphides, chlorides, and cyanides should be absent. According to Krauch [1] commercial "chemically pure" liquor ammonia must comply with the following tests :—

1. *Pyridine and Chlorides.* 10 ml., diluted with 30 ml. water, should remain colourless after being strongly acidified with nitric acid, and should show no change on the addition of silver nitrate solution.

[1] *Prüfung der Chemischen Reagentien auf Reinheit*, 2nd edition, p. 164.

2. *Volatility.* 15 ml., on evaporation in a porcelain crucible, should leave only slight traces of a residue.

3. *Metals.* No change in the appearance of the ammonia solution should be obtained on the addition of 20 ml. of water and a few drops of ammonium sulphide solution to 5 ml. of the ammonia.

4. *Sulphuric Acid.* 10 ml., after being acidified with acetic acid, should yield no precipitate with barium chloride solution, even after prolonged standing.

5. *Carbonic Acid.* 10 ml., on being mixed with 10 ml. of water and 40 ml. of lime water, should yield no turbidity.

3. **Empyreumatic Ingredients.**—Ammonia solutions are seldom completely free from compounds of a pyridine nature, which impart to it an unpleasant odour, and which are also regarded as the cause of the occasional darkening of the originally clear solution.

By dipping a piece of filter paper in the ammonia to be examined, the empyreumatic odour may be perceived after the ammonia has volatilized, but in a short time the former also disappears. The odour is more readily perceptible if a small sample of the liquid is neutralized with sulphuric acid. Pfeiffer adds litmus tincture to the sample, slightly acidifies it, and then throws a little precipitated calcium carbonate into the liquid to take up the excess of acid.

E. Liquefied Ammonia

The liquid ammonia supplied commercially in steel cylinders under pressure as liquefied ammonia is by no means a pure chemical product. It generally contains small quantities of water and organic substances which have been identified by Lange and Hertz [1] as consisting mainly of pyridine, acetonitrile, ethyl alcohol, and a little machine oil. The presence of these impurities, which may amount to about 2 per cent., is under certain circumstances detrimental to the use of liquid ammonia, and it is therefore of importance to determine them analytically, or at any rate to estimate their total amount. The ordinary determinations of the concentration as made in testing ammonia solutions are, of course, not applicable. The usual procedure is to allow a sample of the liquefied gas to evaporate spontaneously under specified conditions, and to determine the non-gaseous residue either gravimetrically or volumetrically.

The analysis of anhydrous ammonia is discussed by Lucian and Prepe.[2] The authors employ for its analysis a modification of Bunte and Eitner's method.[3] About 160 to 170 g. of the liquid ammonia is placed in a Kroecker bomb, and the gas issuing is very slowly passed through three large U-tubes containing sodium hydroxide into a

[1] *Z. angew. Chem.*, 1897, **10**, 224.
[2] *Bull. Soc. Chim. Belg.*, 1906, p. 347; *Z. angew. Chem.*, 1908, p. 497.
[3] *J. Gasbeleucht.*, 1897, **40**, 174.

measured quantity of $N/2$ sulphuric acid solution, contained in two bottles of 3·5 litres capacity, connected in series. When the whole of the liquid ammonia has been passed through the system, air, free from carbon dioxide, is passed through the apparatus and the bomb then heated on a water-bath for thirty minutes. The carbon dioxide present in the sample is determined by passing a second volume of the sample through sodium hydroxide solution.

For the purpose of testing deliveries of liquid ammonia, the following simplified method, due to Lange and Hertz,[1] is commonly employed. To a glass tube 30 to 40 mm. in width, a narrow tube of about 5 mm. in width is fused, which is closed at the lower end (Fig. 20); the total capacity of the tube is about 80 to 100 ml. A mark is placed on the tube corresponding to a content of 49 ml. = 33 g. of liquid ammonia, and the narrow portion is graduated into fifteen divisions, the total volume of the fifteen divisions being 1 ml.; each of these divisions corresponds to 0·2 per cent. by volume, on the assumption that the sp. gr. of liquid ammonia is 0·68 at —38° and that of the residue 0·9 at 15°. To take a sample, the ammonia cylinder is placed in a horizontal position, the valve opened slightly, and the liquid allowed to flow into the tube until it reaches the 49 ml. mark. The liquid is then allowed to evaporate spontaneously, which requires about three hours, a cork and glass tube being placed, if desired, at the top of the tube, and the evolved ammonia led into water. As soon as evaporation is complete and the ice layer which forms on the outside of the tube has thawed, the volume of residue is read off. The method is naturally only an approximate one, and tends to give rather too high results as some ammonia evaporates during the taking of the sample, the high boiling impurities tend to accumulate in the sample actually measured, and the residue always contains ammonia. These errors are partly compensated for owing to the fact that some of the less volatile impurities evaporate with the ammonia, and the results are accordingly sufficiently accurate for most purposes.

FIG. 20.

II. AMMONIUM SALTS

In the manufacture of ammonium sulphate the free ammonia is, in the first instance, distilled off with steam, lime being subsequently added for the decomposition of the fixed salts. The mixture of ammonia, steam, carbon dioxide, hydrogen sulphide, hydrocyanic acid and other impurities is passed through a saturator charged with

[1] *Z. angew. Chem.*, 1897, **10**, 224.

sulphuric acid, whereby the ammonia is retained and converted into sulphate, which crystallizes continuously, the crystals being removed by steam ejectors. The remaining gases pass through the saturator and, after cooling, are treated for the removal of hydrogen sulphide and hydrocyanic acid, the plan most commonly adopted being to allow them to pass through a purifier containing hydrated oxide of iron. Alternatively they may be taken to a sulphuric acid plant, and the hydrogen sulphide burnt to sulphur dioxide for the production of acid.

The analysis of the effluent liquor from the stills is carried out by the methods described for gas liquor, modified, in the determination of ammonia, by increasing the volume taken for analysis and employing deci-normal in place of normal solutions. It should be noted that the effluent may contain suspended lime, which will result in an incorrect value for the ammonia content. The greater part of the lime may be removed by filtration before determining the ammonia content.

For the analysis of waste gases, methods are given by Linder,[1] in which the amounts of hydrogen sulphide, carbon dioxide and hydrocyanic acid are estimated in a manner analogous to that employed for these constituents in ammoniacal liquids.

The Analysis of Ammonium Salts

Practically the whole of by-product ammonia and a large proportion of synthetic ammonia is recovered in the form of ammonium sulphate, the salt being widely used as an agricultural fertilizer. The majority of sulphate of ammonia used for agricultural purposes is now sold under guarantee of ammonia or nitrogen content. Further it may also be guaranteed to be free from acid and moisture, the presence of these impurities producing a tendency for the crystals to cohere and set to a hard mass. To a much smaller extent the chloride, carbonate, bicarbonate, phosphate and thiocyanate are also manufactured by chemical works from synthetic ammonia and from by-product ammonia purchased from gas-works and coke-ovens.

For the complete analysis of an ammonium salt, 40 g. is dissolved in water, filtered through a dried, tared filter paper, and after washing the latter with water, made up to 1 litre. The insoluble residue is dried and weighed and the percentage of insoluble matter calculated from the nett weight of the precipitate. The solution is then employed for the determination of the soluble constituents, each 25 ml. being equivalent to 1 g. of the original salt. (For the analysis of mixed fertilizers containing ammonium salts, see Vol. III., pp. 496 *et seq.*)

[1] *Report on Alkali, etc., Works*, 1906, p. 52.

Ammonium Sulphate.—*Moisture.* 10 g. of the salt is heated in an air-oven for two hours at 110°, the loss of weight indicating the amount of moisture present.

Ammonia. This estimation is carried out by distilling 75 ml. of the solution prepared as above (= 3 g. of the salt) with sodium hydroxide, and collecting the distillate in 50 ml. of standard sulphuric acid in the manner described under gas liquor (p. 69).

1 ml. *N*/1 sulphuric acid ≡ 0·014 g. N.
≡ 0·01703 g. NH_3.

The determination of ammonia by the azotometer (*cf.* Vol. I., p. 75) may also be used, but for exact results the distillation method is preferable.

Percentage Content of Solutions of Ammonium Sulphate at 15° C.*

Per cent. by weight.	Sp. gr.	Per cent. by weight.	Sp. gr.	Per cent. by weight.	Sp. gr.	Per cent. by weight.	Sp. gr.
1	1·0057	14	1·0805	27	1·1554	40	1·2284
2	1·0115	15	1·0862	28	1·1612	41	1·2343
3	1·0172	16	1·0920	29	1·1670	42	1·2402
4	1·0230	17	1·0977	30	1·1724	43	1·2462
5	1·0287	18	1·1035	31	1·1780	44	1·2522
6	1·0345	19	1·1092	32	1·1836	45	1·2583
7	1·0403	20	1·1149	33	1·1892	46	1·2644
8	1·0460	21	1·1207	34	1·1948	47	1·2705
9	1·0518	22	1·1265	35	1·2004	48	1·2766
10	1·0575	23	1·1323	36	1·2060	49	1·2828
11	1·0632	24	1·1381	37	1·2116	50	1·2890
12	1·0690	25	1·1439	38	1·2172	...	...
13	1·0747	26	1·1496	39	1·2228	...	...

* Gerlach, *Z. anal. Chem.*, 1869, **8**, 287.

Acidity or Alkalinity. 50 g. of the salt is dissolved in distilled water previously made neutral to methyl orange, made up to 150 ml. and filtered. 75 ml. (=25 g. of salt) of the filtrate is then titrated with *N*/10 sodium hydroxide, using methyl orange as indicator.

1 ml. *N*/10 sodium hydroxide ≡ 0·0049 g. H_2SO_4.

If the solution is alkaline in reaction, then the titration is carried out with *N*/10 sulphuric acid solution.

1 ml. *N*/10 sulphuric acid ≡ 0·0017 g. NH_3.

Residue on Ignition. 2 g. of the salt is carefully volatilized in a covered platinum crucible, and the residue weighed.

Ammonium Chloride (Sal Ammoniac).—*Percentage Content of Solutions at* 15°. The following table gives the strengths of solutions of different sp. grs., according to Gerlach, Lunge, and Kohler.[1]

[1] Gerlach, *Z. anal. Chem.*, 1869, **8**, 281.

Per cent. NH_4Cl by weight.	Sp. gr.	Per cent. NH_4Cl by weight.	Sp. gr.	Per cent. NH_4Cl by weight.	Sp. gr.	Per cent. NH_4Cl by weight.	Sp. gr.
1	1·00316	8	1·02481	15	1·04524	22	1·06479
2	1·00632	9	1·02781	16	1·04805	23	1·06754
3	1·00948	10	1·03081	17	1·05086	24	1·07029
4	1·01264	11	1·03370	18	1·05367	25	1·07304
5	1·01580	12	1·03658	19	1·05648	26	1·07575
6	1·01880	13	1·03947	20	1·05929	...	...
7	1·02180	14	1·04325	21	1·06204	...	...

The percentages of ammonia, moisture, free acid, insoluble matter, and residue on ignition are estimated in the same manner as in the sulphate.

Chlorine. This is most readily determined by titrating 5 ml. of the solution (40 g. per litre) with neutral *N*/10 silver nitrate, using potassium chromate as indicator. Each ml. of *N*/10 silver nitrate ≡ 0·003546 g. Cl.

Iron. This impurity is sometimes present in commercial sal ammoniac, and is detrimental to its employment in the colour and battery industries. The iron content can be determined by dissolving 25 g. in distilled water, adding 5 ml. of hydrochloric acid and 10 ml. of 20 vol. hydrogen peroxide solution, and boiling for thirty minutes. The solution is then filtered and the filtrate treated with an excess of ammonia solution. After warming for ten minutes, the precipitated iron hydroxide is filtered off, washed with hot water, re-dissolved in dilute sulphuric acid solution, and pure zinc added. When the reduction of the iron is complete, the solution is filtered rapidly through a glass wool filter and titrated against *N*/30 potassium permanganate solution until a faint, permanent pink colour is obtained.

1 ml. *N*/30 potassium permanganate solution ≡ 0·00186 g. Fe.

Ammonium Carbonate.—Commercial ammonium carbonate is a mixture of ammonium carbamate, $NH_2CO \cdot ONH_4$, and ammonium bicarbonate, NH_4HCO_3; it effloresces in the air, losing ammonia, carbon dioxide, and water, and leaving a residue of ammonium bicarbonate. The commercial product, when freshly prepared, usually contains about 30 per cent. of ammonia.

Percentage Content of Solutions at 15°. The following table, due to Lunge and Smith,[1] gives the sp. gr. of solutions of commercial carbonate, the dry salt having the following composition :—

Ammonia	31·3 per cent.
Carbon dioxide	56·6 ,,
Water	12·1 ,,

[1] *J. Soc. Chem. Ind.*, 1883, **2**, 80.

Degrees Twaddel.	Sp gr. at 15°.	Per cent. of ammonium carbonate by weight.	Alteration of sp. gr. for +1°.	Degrees Twaddel.	Sp. gr. at 15°.	Per cent. of ammonium carbonate by weight.	Alteration of sp. gr. for ±1°.
1	1·005	1·66	0·0002	15	1·075	22·25	0·0006
2	1·010	3·18	0·0002	16	1·080	23·78	0·0006
3	1·015	4·60	0·0003	17	1·085	25·31	0·0006
4	1·020	6·04	0·0003	18	1·090	26·82	0·0007
5	1·025	7·49	0·0003	19	1·095	28·33	0·0007
6	1·030	8·93	0·0004	20	1·100	29·93	0·0007
7	1·035	10·35	0·0004	21	1·105	31·77	0·0007
8	1·040	11·86	0·0004	22	1·110	33·45	0·0007
9	1·045	13·36	0·0005	23	1·115	35·08	0·0007
10	1·050	14·83	0·0005	24	1·120	36·88	0·0007
11	1·055	16·16	0·0005	25	1·125	38·71	0·0007
12	1·060	17·70	0·0005	26	1·130	40·34	0·0007
13	1·065	19·18	0·0005	27	1·135	42·20	0·0007
14	1·070	20·70	0·0005	28	1·140	44·29	0·0007

Insoluble matter and the residue on ignition may be determined as in the sulphate. The ammonia may also be estimated by distillation in the usual manner, or the solution may be titrated directly with normal acid solution, using methyl orange as indicator.

Ammonium Nitrate.—In addition to ammonia, the estimation of the nitric acid, and of the nitrous acid, which is frequently present in the commercial salt, may be required.

Nitric acid is estimated as described in Vol. I., pp. 473 *et seq.*, the methods most frequently employed being those of Ulsch, Schlosing-Grandeau, and Lunge.

Nitrous acid is estimated qualitatively in the manner described in Vol. III., p. 407 ; when present only in small amounts, colorimetric methods are used (Vol. I., p. 449). If the quantity is too large for colorimetric estimation, which is seldom the case, the nitrous acid is determined by titration with potassium permanganate solution.

Ammonium Thiocyanate (Sulphocyanide).—This salt is now rarely recovered from spent oxide, but is being obtained as a by-product of the Thylox process of hydrogen sulphide removal from coal-gas. It can be prepared synthetically by the combination of carbon disulphide with ammonium sulphide, and the conversion of the thiocarbonate formed into thiocyanate. The amounts of ammonia and thiocyanic acid present in the salt can be determined by methods quoted under the analysis of gas liquor (pp. 69, 72).

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COAL TAR AND TAR PRODUCTS

By A. McCulloch, M.Sc.(Tech.), A.I.C., and R. M. Drake, M.Sc.

A. RAW MATERIALS

The different classes of coal tar are :—

1. *Low-temperature Tar.* The amount of tar produced by the low-temperature carbonization of coal in 1937 was approximately 8 million gallons. In addition nearly 1½ million gallons of crude spirit was stripped from the gas. The average yield of tar per ton of coal carbonized was 17·1 gallons and 3·07 gallons of crude spirit was recovered. Crude spirit was, however, not recovered in all cases. Low-temperature tar is worked up by the usual methods of distillation, but may also be hydrogenated or cracked. It differs fundamentally in nature and composition from high-temperature tar, and a new technique involving the use of solvents and the avoidance of high temperatures may result in the manufacture of new products.

Vacuum Tar, recovered during the carbonization of coal under much reduced pressures at temperatures below about 450°, has only been produced experimentally.

2. *Peat Tar* is produced, in small quantities only, by methods similar to those employed for the carbonization of coal. The cost of preparation of the peat renders carbonization uneconomic.

3. *Lignite Tar* is obtained from the low-temperature carbonization of lignites and brown coals, especially in Germany, where this industry is firmly established.

4. *Gas Tar.* The Gas Industry supplies approximately 70 per cent. of the total tar produced in Great Britain. Of this quantity some 4 per cent. may be regarded as water-gas tar ; a relatively small amount of coke-oven tar and tars from inclined and intermittent vertical gas retorts is also included. The remainder consists, as far as can be ascertained, of approximately equal quantities of horizontal retort tar and continuous vertical retort tar.

5. *Coke-Oven Tar.* The Coke-Oven Industry provides approximately 29 per cent. of the total tar produced in Great Britain. In the United States, where coke-oven plants are favoured for the manufacture of town gas, this figure rises to as much as 78 per cent.

6. *Blast-Furnace Tar.* In certain localities in Scotland "splint" coals of non-coking character are occasionally used instead of blast-

furnace coke, and here small quantities of blast-furnace tar are recovered. The insignificance of this source of supply is indicated in that, of the 183,276 tons of tar distilled in Scotland in 1938, only 3156 tons are scheduled as produced in iron works. In 1932 no blast-furnace tar was, apparently, produced.

7. *Producer Tar* is recovered from producer-gas plants of large capacity designed for the gasification of bituminous coal. Such plants are used for power generation and for the production of large volumes of gas for heating purposes, especially in the iron and steel industry.

8. *Water-Gas Tar.* The cracking of gas-oil in carburetted water-gas plants for the enrichment of the blue water-gas gives water-gas tar.

9. *Oil-Gas Tar.* In the manufacture of oil-gas, mainly for illuminating purposes, oil-gas tar is produced by the thermal decomposition of oils and petroleum residues without the use of coal or coke.

10. *Bergius Tar.* Material of a tarry nature is produced by the Bergius process in which coal is hydrogenated in autoclaves under high pressures and at temperatures up to 500°. The hydrogenation of coal was established on a commercial scale in England in October 1935. Coal tars of various types have also been subjected to this process with a view to producing low boiling spirits suitable as fuel for internal combustion engines and as solvents,[1] and fuel oils for use in Diesel engines.[2]

Blakeley [3] has proposed a classification of tars on the basis of specific gravity and viscosity. An approximate classification of tars is also stated to be possible on the basis of specific gravity and the yield of distillate at 300°.

I. PROPERTIES AND COMPOSITION OF COAL TAR

True low-temperature tars are usually dark-brown liquids which are quite fluid at ordinary temperatures. In thin layers they are coloured orange to red, and when freshly prepared they possess an odour of hydrogen sulphide and of phenols. Low-temperature tars from lignites and brown coals may be solid at ordinary temperatures owing to the presence of large amounts of paraffin waxes. The viscosity of individual samples may show marked variations due to the varying amounts of waxes, and of resinous and asphaltic substances present in the tar.

High-temperature tar is of more or less viscous consistency and

[1] *J. Inst. Fuel*, 1935, **9**, 65; Gordon, *ibid.*, 1935, **9**, 69.

[2] *Fuel Research Board*, Annual Reports, 1933, 74; 1934, 73; 1935, 91; 1936, 105; 1937, 107; 17th Annual Report, Secretary for Mines, 1937.

[3] *J. Soc. Chem. Ind.*, 1938, **87**, 7.

usually black in colour, with a characteristic odour somewhat similar to that of creosote. Its viscosity is due to the presence of such solid hydrocarbons as naphthalene and phenanthrene and its high free-carbon content. This tar contains relatively simple bodies formed by the thermal decomposition of the complex aromatic and naphthenic hydrocarbons, phenols, bases, and the neutral, phenolic, basic and acidic resinous compounds which constitute low-temperature tar. In general the resinous compounds of all classes of tar disappear as the temperature of carbonization increases, tending to be replaced by the sparingly soluble and more highly condensed materials which constitute the free-carbon in the tar. The free-carbon content is thus broadly an index of the degree of thermal decomposition which the tar has undergone and hence of its manner of production.

The quantity of tar produced and its properties depend upon the nature and size of the coal used, the temperature of carbonization, the rate of heating of the coal, and the time during which the tar vapours are exposed to temperatures higher than that of their formation. Generally speaking, active decomposition of the coal (as shown by the appearance of tar and large volumes of gas) occurs at increasing temperatures the older and more mature the coal. Tar formation commences with peat at about 180°, with lignites at 230° to 260°, with bituminous coals at 300° to 330°, whilst in the case of anthracites active decomposition may be considered to occur at about 330° to 350° with the production of little tar.[1] With bituminous coals, the greater the percentage of oxygen in the coal the greater will be the yield of tar.[2] By slow heating of the coal, tar is driven off completely below 500°, the semi-coke so obtained not yielding further tar on heating.[3]

The effect of the character of the coal on the composition of the tar is illustrated by the special concession given to Scottish creosote for which no upper limit for tar-acid content is specified, the high phenol content of Scottish creosote being attributable to the high oxygen content of Scottish coals.[4]

The amount of tar produced from bituminous coals on carbonization under industrial conditions at varying temperatures rises to a maximum between 500° and 550° and then decreases with increasing temperature.[5]

Low yields of tar at high temperatures are due to secondary thermal decomposition of primary tar produced at low temperatures. The yield of tar by weight and its total thermal content increase rapidly to a maximum with increased rate of heating and then diminishes, secondary thermal decomposition being at its maximum with the

[1] E. C. Jones, *J. Franklin Inst.*, London, 1914, **177**, 511, 5th edition, London.
[2] Lunge, *Coal Tar and Ammonia*, 1916, London, p. 51.
[3] Akira Shimomura, *Fuel*, 1928, **7**, 119.
[4] Cf. *British Standards Institution*, *B.S.* 144, 1936.
[5] *Fuel Research Board*, Technical Paper No. 32, 1931.

most rapid heating of the coal.[1] With increasing temperature the naphthenes, paraffins, complex aromatic and unsaturated hydrocarbons, and the complex tar acids and bases of low-temperature tar are decomposed to produce a characteristic high-temperature tar containing relatively simple aromatic bodies, whilst the pitch and free-carbon contents are considerably augmented.[2]

The influence of carbonizing temperatures on the composition of the tar is shown in the following table [3] :—

Tar from Mitchell Main Coal

Carbonizing temperature	400°	450°	500°	550°	600°	650°	700°	800°	900°
Specific gravity at 15°	0·959	0·980	1·005	1·028	1·062	1·081	1·100	1·162	1·182
Per cent. free-carbon content of tar	0·4	0·2	0·2	0·7	2·3	1·8	3·1	10·4	13·9
Per cent. free-carbon content of pitch	1·9	3·1	16·2	23·0	21·5	33·0	31·9	42·4	30·5
Distillation of tar. Per cent. on tar up to 170°	5·2	5·6	8·6	5·7	5·6	4·3	4·1	2·0	2·4
170° to 230°	23·9	19·0	19·8	17·6	15·3	16·5	14·7	3·9	9·3
230° „ 270°	15·5	14·2	14·1	13·2	11·1	10·3	10·3	9·4	5·4
270° „ 360°	28·9	28·5	29·7	28·7	27·1	25·8	24·6	21·0	17·1
Pitch	25·2	32·0	27·3	34·7	40·7	42·1	45·6	62·4	65·0
Loss	1·3	0·7	0·5	0·1	0·2	1·0	0·7	1·3	0·8

Differences in the composition of tars produced by high-temperature carbonization in continuous vertical retorts and tars obtained from horizontal retorts are due to the more rapid removal of the former through zones of decreasing temperature, so that secondary thermal decomposition is minimised. Continuous vertical retort tars may be

Test.	1.	2.	3.	4.	5.
Temperature of carbonization	1115°-1211°	978°-1193°	1129-°1177°	1128°-1186°	1090°-1096°
Coal per retort per day, tons	3·13	3·28	3·71	3·44	3·10
Steam passed into retort, per cent. weight of coal	nil.	13·3	22·1	32·7	44·8
Tar (dry), gals. per ton	13·2	16·4	16·8	20·4	21·2
Calorific value (gross) of dry tar in B.Th.U. per lb.	16,450	16,230	15,900	16,150	16,130
Specific gravity of tar at 15·5° C.	1·083	1·083	1·082	1·081	1·082
Free-carbon in tar, per cent. by weight	1·5	1·3	1·1	0·7	0·4

[1] Evans, *J. Soc. Arts*, 1923-24, **72**, 767, 785, 805.

[2] *Loc. cit.*: Pictet and Bouvier, *Ber.* 1913, **46**, 3342; Gelsenkirchener Bergwerks-A-G., Abt. Schalke, Austrian Pat. 101681/1924; Kosaka, *J. Fuel Soc.* (*Japan*), 1928, **7**, 1219; Kosaka and Oshima, *Proc. Intern. Conf. Bit. Coal*, 1926, 463.

[3] *Fuel Research Board*, Technical Paper No. 32, 1931.

classed as intermediate between tars from high-temperature horizontal retorts and true low-temperature tars. Steaming of the charge in continuous vertical retorts increases the yield of tar,[1] as shown in the preceding table.

The Fuel Research Board find the yield of tar in continuous vertical retorts 50 per cent. greater with large than small coal. Carbonization of five grades of sizes under identical conditions in a high-temperature horizontal retort showed that the yield of tar progressively decreased as the size of the coal was diminished. Concomitantly, the naphthalene and free-carbon contents of the tars increased.[2] [3]

According to Rhead [4] sized coal of 3 in. to 1¼ in. yielded 17 gals. of tar per ton of coal on carbonization with 10 per cent. steaming, whereas when carbonized under the same conditions after pulverizing, so that 90 per cent. was below 2 in., the yield of tar was reduced to 13 gals.

II. CHARACTERISTICS OF TARS

(a) Low-Temperature Tars

1. **Vacuum Tar** is not produced commercially. Pictet and Bouvier [5] obtained 4 per cent. of a clear light brown tar with a slight green fluorescence on distillation of a French bituminous coal at 15 to 18 mm. pressure up to a temperature of 430°. It had an odour of crude petroleum. The composition of the tar when fresh was as follows :—

	Per cent. of tar.
Bases	0·2
Alcohols	2·0
Saturated hydrocarbons	30·0
Unsaturated hydrocarbons	68·0

Fractional distillation of the saturated hydrocarbons, after removal of the unsaturated hydrocarbons with liquid sulphur dioxide, resulted in the isolation of homologues of cyclohexane, and a small amount of a solid hydrocarbon $C_{30}H_{60}$ (m.p. 62° to 63°). The unsaturated compounds also appeared to be cyclic. Naphthalene and anthracene were absent. Spontaneous decomposition of alcohols resulted in the formation of phenols and cresols after prolonged storage. The absence of phenolic compounds in the freshly obtained tar contrasts

[1] *Trans. Inst. Gas. Eng.*, Fourth Report; *Gas J.*, 1920, **150**, 604; cf. *Fuel Research Board Report*, 1920-21.

[2] *Fuel Research Board*, Technical Paper No. 26, 1930.

[3] *Cf.* Sixteenth Report, Inst. Gas. Eng., *Gas J.*, 1926, **175**, 802.

[4] *Gas J.*, 1926, **175**, 843.

[5] *Ber.*, 1913, **46**, 3342; 1915, **48**, 926; *Compt. rend.*, 1915, **160**, 629; *Chem.-Ztg.* 1914, **38**, 1025; Pictet, Kaiser and Labouchère, *Compt. rend.*, 1917, **165**, 113, 358.

with the results reported by Jones and Wheeler.[1] Vacuum distillation of two British bituminous coals up to 450° gave 6·5 per cent. of a light brown tar of sp. gr. 0·967 to 0·999, 15°/15°, containing 40 to 45 per cent. of unsaturated hydrocarbons, 40 per cent. of naphthenes and liquid paraffins (with naphthenes predominating), 12 to 15 per cent. of phenols consisting mainly of cresols and xylenols, aromatic compounds considered to be homologues of naphthalene, traces of pyridine bases and traces of a solid paraffin $C_{27}H_{56}$. Benzene and its homologues, naphthalene, anthracene, phenanthrene and solid aromatic bodies were generally absent.

Schneider and Tropsch [2] obtained by vacuum distillation of a lignite a tar with a solidification point of 53°, consisting of partly decomposed montan wax and quantities of viscous oils. The cracking of the vacuum tar, recovered by Jones and Wheeler (*loc. cit.*) at atmospheric pressure and a temperature of 650°, gave a tar weighing 55 per cent. of that of the original tar, with a sp. gr. of 1·043, 15°/15°, and a higher carbon content.[3] Jones concluded that the naphthenes, paraffins, and unsaturated hydrocarbons in the tar decomposed to form olefines of varying carbon content, which condensed at high temperatures forming aromatic substances.

2. **Low-Temperature Tars,** produced from bituminous coals by carbonization between 450° and 650°, are usually dark brown in the mass, and orange to red in thin layers. Their specific gravities are considerably lower than those of high-temperature tars, ranging from about 0·95 to 1·06 at 25°, compared with about 1·2 for the latter.[4] The low sp. gr. is due to the absence of solid hydrocarbons, such as naphthalene and anthracene and the presence of compounds richer in hydrogen. Low-temperature tars from lignites may be solid at ordinary temperatures owing to a high content of solid paraffins. Those from bituminous coals are usually mobile at normal temperatures, although the viscosities of individual samples may vary considerably owing to varying amounts of resinous and asphaltic substances. The viscosity of the tar as recovered satisfies fuel oil requirements, but the flash point is too low, and if topped to remove light spirit the tars become too thick for this purpose.[5] The viscosity may increase owing to oxidation of the tar during storage.[6] Wide variation is found in the composition of different low-temperature tars and in their behaviour on distillation, certain constituents decomposing above 150°. The yield of low-temperature tar and its content of

[1] *J. Chem. Soc.*, 1914, **105**, 140, 2562.
[2] *Abh. Kohle*, 1917, **2**, 28.
[3] Jones, *J. Soc. Chem. Ind.*, 1917, **36**, 3.
[4] Fischer, *Z. angew. Chem.*, 1919, **32**, 337.
[5] Lander and McKay, *Low Temperature Carbonisation*, London, 1924, p. 170.
[6] Parr and Olin, *Eng. Expt. Stat.*, *University of Illinois*, *Bulls.* 60, 1912; 79, 1915.

phenols increases the younger the coal from which it is produced.[1] Cracking of a tar will be increased if the coal fuses during carbonization.

Two general methods of examination have been employed: distillation of the tar in a manner similar to that of high-temperature tar, and preliminary treatment with solvents followed by distillation. According to the former, low-temperature tars contain 50 to 80 per cent. of neutral oil, which consists of paraffin, naphthenic, aromatic and unsaturated hydrocarbons, together with oxygen and sulphur compounds. The paraffins and naphthenes are greatest in amount in the lowest fractions and do not form more than 20 per cent. of the neutral oil. In the fractions between 100° and 300° they constitute 10 to 15 per cent.; above 300° the amount may increase if considerable quantities of solid paraffins are present, as in tars from lignites and brown coals.

Aromatic hydrocarbons of unknown composition appear to constitute about 40 to 50 per cent. of the oil distilling above 200°. Homologues of benzene, naphthalene and anthracene occur, but the parent bodies are present only in small amounts. Unsaturated hydrocarbons of an open-chain type predominate in the lowest fractions, and cyclic unsaturated hydrocarbons in the middle and highest fractions of the neutral oil. Certain of these readily oxidize, so that the distillates darken rapidly on exposure to air. The high-boiling hydrocarbons are very viscous and tend to resinify. Phenols may constitute 10 to 50 per cent. of the tar, depending mainly on the oxygen content of the coal, and comprise cresols, xylenols and high-boiling unstable resinous bodies. Phenol is present only in small quantities. Naphthols and catechol have been detected, but phenol ethers appear to be absent. Carboxylic acids may also occur in small amounts. Sulphur and nitrogen compounds also appear in the separated phenols. Up to 5 per cent. of bases may be present, consisting of homologues of pyridine and quinoline, hydrogenated derivatives of these compounds and viscous high-boiling resinous bases. Aniline and pyridine are present only in small quantities. Sulphur compounds may constitute as much as 10 per cent. of the tar, and hydrogen sulphide is always evolved on distillation. Acetone has been identified in certain tars, but the nature of the higher boiling ketones is unknown. The literature of low-temperature tar has been treated fully by Parrish [2] and Gentry.[3]

Preliminary treatment of low-temperature tar with solvents is exemplified in the work of Morgan and his collaborators.[4] The

[1] Fischer, *Brennstoff-Chem.*, 1923, **4**, 51.
[2] *Fuel*, 1926, **5**, 436.
[3] *The Technology of Low-Temperature Carbonisation*, London, 1928.
[4] *J. Soc. Chem. Ind.*, 1928, **47**, 131 T; 1929, **48**, 29 T; 1932, **51**, 67 T. *Chim. et Ind.*, 1928, **19**, No. 6; *Fuel*, 1931, **10**, 183; 1935, **54**, 19 T.

constituents of low-temperature tars are divisible into crystalloids (which include neutral oils), waxes, bases and mono- and polycyclic aromatic hydrocarbons, and resinoids which are non-crystallizable amorphous substances of neutral, basic, phenolic and acidic character. Initial separation is effected by successive treatments with aqueous alkalis and dilute mineral acids, these separated fractions being each subsequently extracted with organic solvents. The neutral oil is distilled up to 120° under 2 mm. pressure, the least volatile portions of the oil being treated with various solvents.

Morgan gives the following table of substances identified in low-temperature tar by the above procedure.

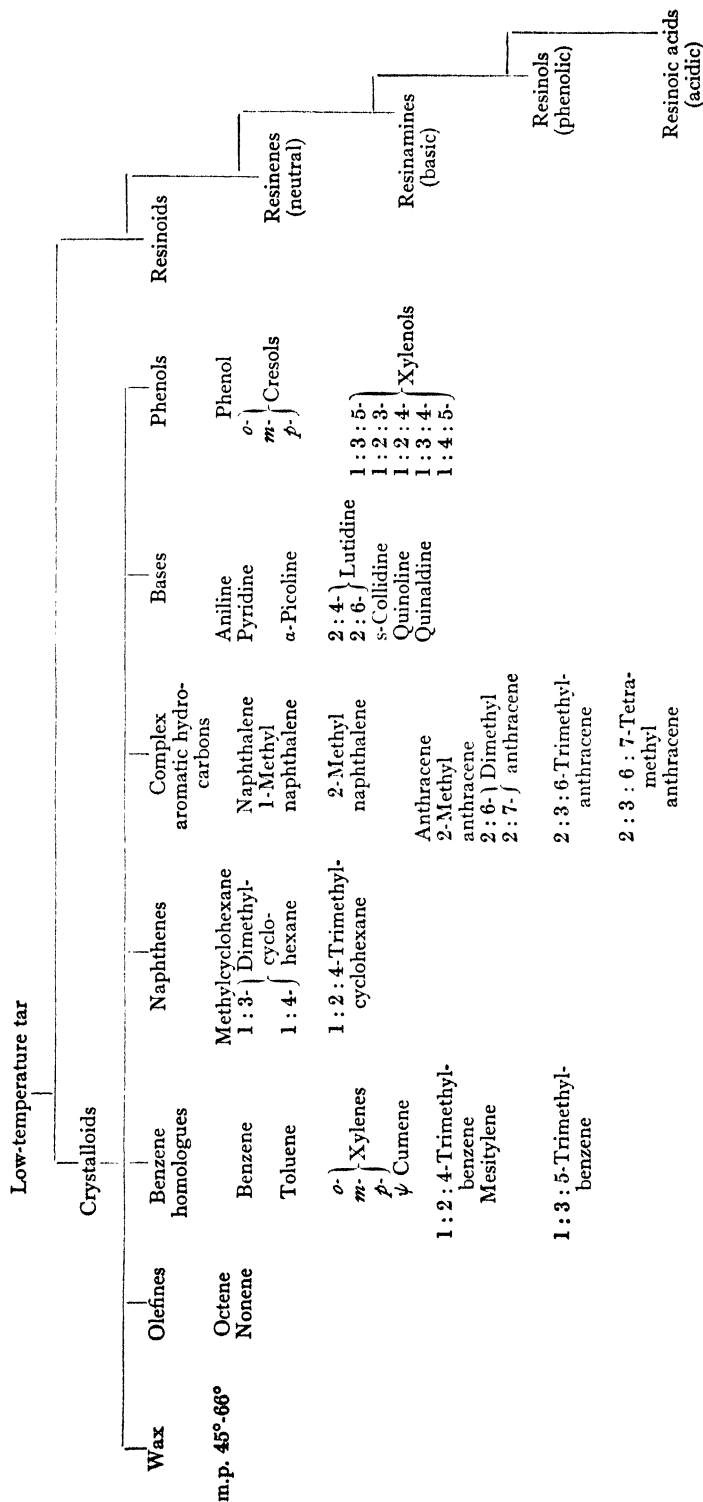
The resinoids of low-temperature tar are pale yellow to brown amorphous powders precipitated from solution in organic media by the addition of light petroleum. The amount of material in low-temperature tars insoluble in common organic solvents such as benzene, ether, and chloroform is usually less than 1 per cent. In this respect they differ from high-temperature tars, the latter containing the so-called free-carbon, insoluble in benzene and toluene and amounting to 20 per cent. or more.

The quantity of pitchy substances precipitated from low-temperature tars on addition of petroleum ether varies greatly, amounting in extreme cases to 50 per cent. Certain investigators term this material asphalt, and it may be found not only in the neutral oils but, as indicated above, be basic, phenolic or acidic in nature. Such bodies, described variously by Marcusson and Picard,[1] Edwards,[2] Tropsch,[3] Brittain, Rowe and Sinnatt,[4] Parrish and Rowe,[5] and Weindel,[6] approximate to the resinoids of Morgan. The latter are of high molecular weight and dissolve in alcohols, acetone, chloroform and benzene ; on evaporating their solutions hard transparent resinous films remain. They are all present in varying amount in both low- and high-temperature tars from wood, peat, lignite and bituminous coal. In general all classes of resinoids diminish in amount as the temperature of carbonization increases, tending to be replaced by free-carbon.

With increasing temperatures there is also a diminishing yield of tar, an increase in sp. gr., a higher yield of pitch on distillation, and a diminishing yield of neutral oil, and of basic, phenolic, and acidic constituents.

The results of the examination of seven industrial low-temperature tars are summarized in the table on page 96.

[1] *Z. angew. Chem.*, 1921, **34**, 201 ; 1923, **36**, 253 ; *Brennstoff-Chem.*, 1924, **5**, 68.
[2] *J. Soc. Chem. Ind.*, 1924, **43**, 143 T, 149 T.
[3] *Brennstoff-Chem.*, 1921, **2**, 251.
[4] *Fuel*, 1925, **4**, 263, 299, 337.
[5] *J. Soc. Chem. Ind.*, 1926, **45**, 99 T.
[6] *Brennstoff-Chem.*, 1923, **4**, 321.

Low-Temperature Tars

Morgan and Pettet (*J. Soc. Chem. Ind.*, 1935, **54**, 19 T.) have isolated the following phenols from undistilled low-temperature tar: phenol, *o*-, *m*-, and *p*-cresol, *o*-4-, *m*-4-, *m*-5-, and *p*-xylenol, iso-ψ-cumenol, 3-methyl-5-ethyl phenol and β-naphthol, whilst α-naphthol has been identified as the picrate. Morgan and Coulson (*J. Soc. Chem. Ind.*, 1934, **53**, 71 T.) have shown that low-temperature tar and its distillates contain anthracene, 2-methyl-, 2 : 6-dimethyl-, 2 : 3 : 6-trimethyl-, and 2 : 3 : 6 : 7-tetra-methyl anthracene. A constituent of low-temperature distillates which imparts an intense yellow colour to the anthracene hydrocarbons is mainly 2 : 6-dimethylnaphthacene.

Process.	1. Maclaurin.	2. "L. & N."	3. Babcock & Wilcox.	4. Bussey.	5. Turner.		6. Low-Temperature Carbonization Ltd.	7. Fuel Research (Richmond).
Coal carbonized.	Virgin Seam, Uddingston, Lanarkshire.	New Lount, Leicestershire.	Seaton Delaval, Hastings Pit, Northumberland.	Bothwell Castle, Lanarkshire.	Coalburn, Lanarkshire.		Blend of six Durham coals (medium caking).	South Hetton, Durham.
Temperature of carbonization	700°	470°	550°	500°	450° to 500°		585°	640°
Steam admitted to retort (per cent. of *coal as charged*)	20·0	nil	28·0	11·0	130·0		nil	10·1
					"Light tar."	Heavy wax.		
Yield of dry tar: (*a*) Gals. per ton of dry coal	17·8	14·1	16·8	19·8	17·0	6·5	17·6	20·3
(*b*) Kg. per ton of *ash-free dry coal*	86·2	79·6	87·6	99·7	82·3	36·5	88·5	102·5
Specific gravity of tar	1·035	1·12	1·051	1·041	0·983	1·112	1·05	1·042
Residue when distilled to 360°, kg. per ton, *ash-free dry coal*	23·4	32·5	16·9	19·1	20·2	17·6	31·0	21·5
Yields: kg. per ton, ash-free dry coal:								
Neutral oil	50·2	35·9	40·1	59·2	59·1	16·4	51·1	60·1
Wax, m.p. 50°	1·9	1·0	1·8	2·5	1·2	1·7	1·4	0·8
Naphthalene	0·3	0·1	trace	0·3	trace	nil	trace	0·1
Resinenes from neutral oil	4·2	4·5	3·3	2·9	1·0	2·0	1·4	3·0
Bases:								
Crystallizable	3·2	1·4	2·7	2·7	2·1	1·0	3·3	3·9
Resinamines	0·2	0·3	0·4	0·7	0·8	0·3	0·4	1·3
Carboxylic acids:								
Crystallizable	0·4	0·1	0·3	nil	nil	nil	0·6	0·4
Resinoic acids	0·2	0·6	0·4	0·4	0·2	0·3	0·2	0·6
Phenols:								
Crystallizable	15·0	6·5	20·9	17·2	12·6	6·0	11·8	9·9
Resinols	6·3	15·2	6·8	7·9	2·6	4·4	5·7	13·9
Phenolate soluble:								
Crystallizable	0·9	0·4	3·2	2·4	2·2	1·0	2·5	2·2
Resinenes	1·2	3·0	1·5	0·8	0·6	0·3	6·3	1·4
Precipitates:								
(*a*) (by ether from crude tar)	0·2	9·2	3·7	0·8	nil	2·1	0·3	1·4
(*b*) (by acid in extraction of bases)	1·9	1·2	1·0	1·5	0·4	0·9	3·5	3·6

[1] *Fuel Research Board*, Report on Maclaurin Plant, 1929.
[2] *Fuel Research Board*, Report on Leicestershire Coal Distillation Co. Ltd. Plant, 1931.
[3] *Fuel Research Board*, Report on Babcock Low-Temperature Plant, 1930.
[4] *Fuel Research Board*, Report on Bussey Coal Distillation Co. Ltd. Plant, 1931.
[5] *Fuel Research Board*, Report on Turner Retort, 1930.
[6] *Fuel Research Board*, Report on Parker Low-Temperature Carbonization Plant, 1924.
[7] *Fuel Research Board*, Technical Papers No. 7, 1923; No. 17, 1927; Annual Report, 1931.

The Maclaurin plant was similar in shape to a blast furnace, carbonization being effected by partial combustion of the charge, and the volatiles driven off between 200° and 500°. The "L. & N." retort was a 90 ft. × 9 ft. diameter rotating steel cylinder. Producer gas was admitted at 700°, and passed counter to the flow of coal. Oils boiling below 200° had in part escaped condensation. Carbonization in the Babcock & Wilcox plant was effected at 550°, by the heat of combustion of pulverised fuel, producer gas or coke-oven gas, the temperature being controlled by a steam blast.

The Bussey plant was of a producer type with steam-air blast, a temperature of 500° obtaining. The "Turner" tar was produced in a vertical retort internally heated with superheated steam, the distillates being fractionally condensed. Low Temperature Carbonisation Ltd. used a cast-iron cylindrical block containing twelve vertical retorts, each with a capacity of 50 lb. of coal, the blocks being heated externally with producer gas. In the Richmond installation of Fuel Research Board Retorts the retorts were of a vertical type and constructed of cast-iron, and were externally heated with producer gas. Superheated steam was admitted at the base.

Bristow [1] gives data on the specific gravity, water content, flash point, fire point, viscosity, tar acid content, boiling range, free-carbon (insoluble in benzole), carbon residue (Conradson test), calorific value, sulphur and octane number respectively for crude coal oil prepared by the "Coalite" process of low-temperature carbonization and a large range of distillation products and products specially prepared to meet specification requirements.

Yields and distillation ranges of a variety of low-temperature tars are given below [2] :—

Name of retort.	"Coalite" Parker.	Midland coal products (pitch briquettes).	Fusion Rotary (Cannel).	Freeman Multiple.	Crozier retort.	Maclaurin plant.	Fuel Research Board.	Babcock plant.	Turner plant.
Yield of tar (gals. per ton)	18·6	21·0	50·2	21·1	18·8	17·8	17·3	16·8	22·1
Specific gravity	1·063	1·076	...	1·057	1·028	1·035	1·050	1·051	0·998
Spirit from gas (gals. per ton)	1·78	...	3·7	0·85	0·80	...	1·4	2·6	2·0
Up to 170°	4·7	1·1	...	6·9	4·1	1·1	3·4	0·5	3·4
170° ,, 230°	14·9	3·9	...	9·5	11·7	13·9	14·7	5·6	12·0
230° ,, 270°	12·9	4·1	...	13·9	11·9	16·0	11·1	13·1	14·4
270° ,, 310°	18·1	...	...	...	...	12·8	...	11·1	13·9
270° ,, 330°	...	...	...	...	15·7	...	...	...	...
270° ,, 345°	...	...	...	...	...	...	23·4	...	...
270° ,, 360°	...	26·9	...	29·8	...	...	...	...	...
310° ,, pitch	...	...	...	...	...	20·3	...	28·8	27·2
Pitch	48·4	63·2	...	39·3	55·9	35·1	45·8	40·0	28·7
Loss	1·0	0·8	...	0·6	0·7	0·4	1·6	0·9	0·4
Tar acids	17·0	13·4	...	24·5	14·3	24·0	...	28·0	30·8

[1] *J. Inst. Fuel*, 1936, 10, 43.

[2] *Fuel Research Board*, Technical Paper No. 32, 1931.

Yields on fractionation of a low-temperature tar and its separated products are summarized in the following tables [1] : —

Fractionation of Tar

(Yield per ton of dry coal (Shafton Seam)—25 gals.)

Fraction.	Per cent. by weight of tar.	Yields per ton of dry coal.		Specific gravity of fraction 15°/15°.
		gals.	lb.	
Up to 170°	4·2	1·4	11·6	0·828
170° „ 230°	17·6	4·8	46·0	0·958
230° „ 270°	11·0	2·9	28·7	0·991
270° „ 310°	14·4	3·7	37·6	1·015
310° „ pitch	6·7	1·7	17·5	1·029
Pitch	45·9	...	120·0	...

Fractionation of Tar Acids, Bases, Neutral Oil and Saturated Oil

Fraction.	Tar acids.		Tar bases.		Neutral oil.		Saturated oil.	
	Per cent. by weight of tar acids.	Per cent. by weight of dry tar.	Per cent. by weight of tar bases.	Per cent. by weight of dry tar.	Per cent. by weight of neutral oil.	Per cent. by weight of dry tar.	Per cent. by weight of saturated oil.	Per cent. by weight of dry tar.
Up to 170°	...	...	6·8	0·12	14·9	4·3	10·8	0·7
170° „ 230°	55·9	12·4	26·0	0·44	22·9	6·7	17·4	1·1
230° „ 270°	14·3	3·2	23·4	0·39	20·1	5·9	15·7	1·0
270° „ 310°	10·7	2·4	19·2	0·33	19·9	5·8	15·4	1·0
310° „ 360°	9·6	2·1	11·9	0·20	16·0	4·7	18·5	1·2
Pitch	6·3	1·4	7·3	0·12	5·0	1·5	20·3	1·3
Loss	3·2	0·7	5·4	0·09	1·3	0·4	1·9	0·1

Constitution of Tar Oils

	Per cent. of tar oil.	Per cent. of tar.
Tar acids	41·1	22·2
Polyhydric phenols and carboxylic acids	0·9	0·5
Bases	3·2	1·7
Neutral oil	53·9	29·2
Saturated oil	11·9	6·4
Unsaturated oil (by difference)	42·0	22·8

[1] *Fuel Research Board*, Technical Paper No. 32, 1931.

Treatment of a tar by solution involving the use of ether and petroleum ether successively, followed by separation into acids, bases, unsaturated compounds and refined oil in the usual manner, is contrasted in the following table with similar data obtained after distillation :—

	Method involving Solution.	
	Solution. Per cent.	Distillation. Per cent.
Tar acids	26·2	23·3
Bases	2·7	2·5
Unsaturated compounds	6·6	8·1
Refined oil	41·6	33·6
Precipitate from ether	0·9	...
,, ,, petroleum ether	13·5	...
,, ,, dilute acid	8·1	...
Pitch	...	32·3
Loss	0·4	0·2

33·4 per cent. of the refined oil obtained by solution was volatile at 360° compared with 31·4 per cent. by distillation ; 19·6 per cent. of petroleum ether-soluble tar acids was obtained by solution methods and 19·7 per cent. by distillation ; of tar bases obtained by solution, 76·0 per cent. was volatile at 310°, as compared with 73·2 per cent. by distillation, whilst the amount of completely saturated compounds found in the tar after distillation was practically identical with that found after treatment by solution.

The hydrogenation of low-temperature tar in a single stage process, the refining of hydrogenation spirit, the composition of the products of hydrogenation, the liquid-phase hydrogenation of low-temperature tar and the production of Diesel oil from low-temperature tar are described at length in the Annual Reports of the Fuel Research Board from 1933 to 1937. The cracking of low-temperature tar for the production of motor spirits is discussed in the above Annual Reports and also by Hall and Cawley,[1] and Carlile, Cawley and Hall.[2]

Egloff[3] gives the following results obtained by cracking low-temperature tars in the liquid phase at temperatures of about 450° and pressures of 100 to 250 lbs. per sq. in.

According to Bristow[4] the yield of motor spirit obtained when low-temperature tar is hydrogenated at about 200 atmospheres and a temperature of 450°, using a molybdenum sulphide catalyst is approximately 100 per cent. King[5] gives additional data on tar hydrogenation.

[1] *J. Soc. Chem. Ind.*, 1937, **56**, 303 T. [2] *Ibid.*, 1938, **57**, 240.
[3] *Trans. Fuel Conf. W.P.C.* (London), 1928, **1**, 763 ; *cf.* Rapoport and Kaftanov, *Chem. Abs.*, 1934, 5965.
[4] *J. Inst. Fuel*, 1936, **10**, 43. [5] *Ibid.*, 1932, **6**, 33.

Tar.	West Virginia low-temperature tar.	Ohio-Indiana low-temperature tar.	Utah low-temperature tar.	West Virginia low-temperature neutral oil.	German lignite tar.	German lignite tar distillate.	German lignite tar.
Specific gravity, 60°/60° F.	1·074	1·079	0·983	0·948	0·973	0·927	0·941
Distillation (°C.) 10 per cent.	196·0	208·0	249·0	232·0	301·0	280·0	151·0
Distillation (°C.) 50 per cent.	307·0	348·0	366·0	291·0	357·0	328·0	303·0
Distillation (°C.) 90 per cent.	393·0	...	394·0	368·0	378·0	392·0	370·0
Tar acids	...	27·5	29·0	0·0	19·7	...	22·5
Tar bases	...	1·55	...	0·0	1·0	...	3·0
Sulphur, per cent. by weight	...	...	...	...	...	...	0·49
Cracking conditions :—							
Temperature (°C.)	452	427	435	454	438	454	482
Pressure (lbs. per sq. in.)	100	100	110	250	90	150	200
Yield—total	30·0	34·0	48·4	50·0	64·4	67·1	81·7
Motor spirit	23·0	22·0	24·0	...	38·3	47·4	48·2
Fuel oil (tar acid-free basis)			18·0	...	19·3	17·6	...
Specific gravity, 60°/60° F.	...	...	0·787	...	0·769	0·776	0·783
Initial-point (°C.)	...	...	43	...	44	44	43
End-point (°C.)	...	...	224	...	224	227	216
Sulphur, per cent. by weight	...	...	0·15	...	0·43	0·5	0·45
Benzole equivalent	...	...	65	>50	...	...	...
Octane number	...	...	...	...	...	...	77 (Res. M.)
Coke, lb. per bbl.	...	193	120	84	77	50	(loss 12·3 per cent.)
Gas, cub. ft. per bbl.	...	525	618	840	767	571	...

The average calorific values of low-temperature tars are from 15,500 to 16,500 B.Th.U. per lb. (gross) compared with 18,500 to 19,500 B.Th.U. per lb. (gross) for crude petroleum.[1]

(b) Peat Tar

Peat tar is not produced in commercial quantities owing to the prohibitive cost of drying and briquetting the peat. On carbonization peat yields 2 to 10 per cent. of its weight of the air-dried peat as tar. It is a black viscid liquid with a disagreeable acrid odour. Carbonization of peat in a shaft furnace gave 10 to 13 per cent. of tar containing 15 per cent. of paraffin wax, 15 per cent. of viscous oils, 12 per cent. of non-viscous oils and 41 per cent. of phenols.[2]

Yields of primary tar from different peats are given below [3] :—

Kind of peat.	Primary tar from peat dried at 105°.	Primary tar contains	
		Crude paraffin wax.	Phenols.
	Per cent.	Per cent.	Per cent.
Fuel peat from Velen (Westphalia)	12	...	...
Lauchhammer peat—			
Top layer	18	14	14
Middle layer	17	13	13
Bottom layer	27	17	15

Dry peat tar yields the following on distillation [4] :—

	Crude.	After Purification.
	Per cent.	Per cent.
Light naphtha	16	12
Heavy naphtha	30	25
Lubricating oil	15	13
Paraffin wax	12	2
Peat-tar pitch	16	16
Creosote	...	12
Loss	11	20
	100	100

[1] *Fuel Research Board*, Technical Paper No. 32, 1931.
[2] Steinert, *Z. angew. Chem.*, 1922, **35**, 553.
[3] Fischer and Lessing, *Conversion of Coal into Oils*, London, 1925, p. 27.
[4] Abraham, *Asphalts and Allied Substances*, London, 1938, p. 309.

Abraham[1] gives the following properties of dehydrated peat tars in general :—

Colour in mass	Black.
Specific gravity at 77° F.	0·90 to 1·05
Consistency	Liquid.
Fusing point by Kraemer and Sarnow method	40° to 60° F.
Volatile matter at 500° F. in 5 hours (A.S.T.M.)	50 to 85 per cent.
Flash-point (Pensky-Martens closed test)	60° to 95° F.
Fixed-carbon	5 to 15 per cent.
Solubility in carbon disulphide	98 ,, 100 ,,
Solubility in 88° petroleum naphtha	95 ,, 100 ,,
Sulphur	Less than 1 per cent.
Mineral matter	0 to 1 per cent.
Solid paraffins	5 ,, 15 ,,
Saponifiable constituents	5 ,, 15 ,,

The pitch is obtained by direct or steam distillation, and resembles pitch from lignite tars. It is very susceptible to changes of temperature and does not weather well.

(*c*) Lignite Tar

The nature and yield of lignite tar vary considerably with the nature of the lignite and the method of carbonization or gasification.

Carbonization at low temperatures of three German lignites gave[2] :—

Kind of coal.	Primary tar calculated on coal dried at 105°.	Primary tar contains		
		Paraffin wax.	Phenols.	Viscous neutral oils.
	Per cent.	Per cent.	Per cent.	Per cent.
Saxon coal used for low-temperature carbonization	24·0	29	15	17
Rhenish brown coal	7·6	13	36	15
Lignite	2·7	?	57	?

Carbonization in " Rolle " retorts of special design at 500° to 900° F. of two lignites, one a bituminous lignite containing 20 to 30 per cent. of moisture, and the other a non-bituminous lignite containing 15 per cent. of moisture, yielded respectively 24 per cent.

[1] *Loc. cit.*, p. 310.
[2] Fischer and Lessing, *Conversion of Coal into Oils*, London, 1925, p. 26.

of tar (sp. gr. 0·885/50°, solidifying point 37°), containing 16 per cent. of creosote oils and 7·6 per cent. of tar (sp. gr. 0·955/50°, solidifying point 33°), containing 37 per cent. creosote oils. Steam distillation gave 3·2 per cent. of pitch with the former and 8·5 per cent. with the latter.[1]

Lignite tar in general is of buttery consistency, with a sp. gr. of 0·85 to 1·05 at 77° F. and is dark-brown to black in colour. The tar is usually more paraffinoid than gas or coke-oven tar, and may contain from 10 to 25 per cent. of solid paraffins, ketones as characteristic constituents [2] amounting in the fractions boiling between 110° and 400° to 2·2 to 4·5 per cent.,[3] olefines, higher phenols and their derivatives and small quantities of aromatic constituents. Kabelac,[4] however, states that when produced at temperatures above 900° in horizontal retorts the tar is benzenoid in character and similar to ordinary coal tar. He identified the simple aromatic hydrocarbons, further yields of which he obtained on cracking the fractions at 800°. Lignite tars readily emulsify with water, which separates with difficulty, and when produced by gasification may contain up to 3 per cent. of free-carbon. An average lignite tar yields on distillation, benzine, 5 per cent.; lubricating oil, 5 to 10 per cent.; light paraffin oils, 10 per cent.; heavy paraffin oils, 30 to 50 per cent.; hard paraffin, 10 to 15 per cent.; soft paraffin, 3 to 6 per cent.; dark coloured products, 3 to 5 per cent.; coke, gas and water, 20 to 30 per cent.; or, if distillation is interrupted, lignite tar pitch, 5 per cent.[5]

(*d*) Gas Tar

Gas tar is produced in approximately equal quantities by the carbonization of gas-making coals in continuous vertical retorts and horizontal retorts. Inclined chambers and retorts, and by-product coke ovens account for relatively small quantities. Vertical retort tar is usually distilled in admixture with horizontal retort tar according to normal manufacturing procedure. Differences in the yields and composition of vertical retort and horizontal retort tars are due mainly to the extent to which the primary tar is thermally decomposed, prolonged exposure to high temperatures in horizontal retorts causing the maximum degree of cracking to the more stable aromatic hydrocarbons. The effect of temperature and the character of the

[1] Abraham, *Asphalts and Allied Substances*, London, 1938, p. 315.

[2] Marcusson and Böttger, *Brennstoff-Chem.*, 1922, **3**, 369.

[3] Pfaff and Kreutzer, *Z. angew. Chem.*, 1923, **36**, 437.

[4] Eleventh Report, Fuel Tech. Inst. Czech. Polytech. High School, Prague, 1922, **3**, 84, 89; *cf.* Trutnovsky, *Braunkohle*, 1922, **21**, 445.

[5] Scheithauer, *Die Schwelteere, ihre Gewinnung und Verarbeitung*, Berlin, 1922.

carbonization process upon the yield and characteristics of the tar is shown below.[1]

Process.	Average temperature.	Yield of tar. Gals. per ton.	Specific gravity of tar.	Free-carbon.	Pitch by weight.	Naphthalene.	Paraffin.
						Per cent. in distillate to 360°.	
	°C.			Per cent.	Per cent.		
Ultra-narrow coke-ovens	1300	...	1·210	22·0	72	30 to 35	nil
Ordinary battery ovens .	1000 to 1250	9·5	1·200	14·0	60	20 „ 30	„
Horizontal gas retorts .	900 „ 1200	11·0	1·190	15·0	66	15 „ 20	trace
Inclined gas retorts .	1000 „ 1100	12·0	1·155	6·0	58	...	...
Vertical gas retorts .	1000 „ 1200	15·5	1·080	2·5	48	under 5	13

Vertical retort tars, especially when produced from high oxygen coals, contain large quantities of tar acids and substances which on distillation cause rapid darkening of freshly-distilled cresylic acid and produce red emulsions when the acids are used as disinfectants.

Horizontal retort tars are distinguished by a high sp. gr. (1·15 to 1·25), a high content of free-carbon (16 to 35 per cent.), and high naphthalene and anthracene contents, whilst the light oils are practically devoid of any paraffins. Vertical retort tars are much less viscous, the sp. gr. is from 1·05 to 1·18, and they contain less free-carbon and pitch. The light oil content is higher and the light oil contains appreciable quantities of paraffins. The tars from intermittent and inclined retorts are intermediate in composition between horizontal and continuous vertical retort tars. The tables on pp. 105 and 106 show the differences in distillation range and composition between tars from various retorts.

The yields of finished products from various vertical and horizontal tars, together with comparative data for a low-temperature tar and a narrow coke-oven tar, have been compiled by Macleod, Chapman and Wilson (*loc. cit.*).

Sharples (*loc. cit.*) gives detailed results of rectifying the fractions obtained from the vertical and horizontal tars shown in columns 5 and 6 of the table on p. 105.

(*e*) Coke-Oven Tar

Coke-oven tars vary considerably in nature and composition according to the temperature of carbonization and the type of oven employed. Rapid carbonization, as advocated in modern practice, may produce a tar containing much naphthalene, anthracene and pitch, and very little naphtha. With older coke-oven plants, the tar somewhat resembles the tar produced from lightly-charged horizontal retorts, but is more mobile, the free-carbon content varying from

[1] Macleod, Chapman and Wilson, *J. Soc. Chem. Ind.*, 1926, 45, 401 T.

	Dessau * vertical retort.	Horizontal * retort.	Vertical † retort.	Inclined † retort.	Vertical ‡ retort.	Horizontal ‡ retort.	Vertical § retort.		Horizontal § retort.	
Specific gravity . . .	...	...	...	...	1·075	1·20	1·085	...	1·175	...
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Sp. gr.	Per cent.	Sp. gr.
Ammonia water . . .	2·17	3·50	5·70	10·35	2·42	1·55	2·6	1·018	3·0	1·003
Crude naphtha— Light oil up to 100° } Light oil, 100° to 170° }	5·85	3·10	 { 8·90 { 1·20	 1·00 1·60	 2·44 } 18·55 16·11 }	 2·62 } 12·06 9·44 }	 1·57 10·77	 0·864 0·962	 1·34 6·02	 0·925 1·007
Carbolic oil	...	...	...	...	14·10	12·09	...	...	...	...
Middle oil, 170° to 230° .	12·32	7·68	13·50	7·50	...	...	17·00	0·988	6·18	1·025
Creosote	...	...	...	...	21·47	13·00	...	...	...	...
Heavy oil, 230° to 270° .	11·95	10·15	7·30	10·70	...	...	20·75	1·021	16·32	1·045
Anthracene oil . . .	15·96	11·54	29·30	18·80	...	...	...	...	...	...
Pitch	49·75	62·00	34·10	58·13	43·38	61·30	45·00	1·120	65·56	1·280
Type of coal	English gas coal		...		Scottish gas coal		Scottish coal			

* Bueb, *cf.* Bertelsmann, *Entwicklung der Leuchtgaserzeugung seit*, 1890, p. 39.

† Schäfer, *Einrichtung und Betrieb eines Gaswerkes*, 1910, p. 194.

‡ Sharples, *Gas J.*, 1917, 139, 469.

§ Macleod, Chapman and Wilson (*loc. cit.*).

Coal used.	Maclaurin low-temperature tar.*	New vertical retort tar.	Old horizontal retort tar.	Horizontal tar (high heats).	Horizontal tar.	Ultra-narrow modern coke-oven.
	Lanarkshire gas.	Lanarkshire gas.	Lanarkshire gas.	Lanarkshire gas.	Durham and foreign.	Auchengeich Colliery (Lanark).
Yield of tar (gals. per ton of coal)	16·5	14·8	11·0	10·8	...	6·0
Specific gravity of tar	1·050	1·075	1·180	1·212	1·156	1·264
Product (gals. per ton of tar)—	Sp. gr.	Sp. gr.	Sp. gr.			
Motor spirit	0·05 0·854	0·30 0·858	1·60 0·875	0·04	0·45	...
Light solvent	0·56 0·820	0·28 0·844	1·12	0·25	1·07	...
90/160 solvent	0·66	0·97 0·835	2·66	0·16	0·45	...
90/190 „	1·77	2·23	3·37	0·37	0·75	...
	3·04	3·78	8·75	0·82	2·72	0·30
Unsaturated compounds	1·27	2·10	...	0·31	1·75	...
Pyridine bases	1·79	3·91	1·60	2·73	2·67	trace
Crude tar acids	41·0	18·72	10·56	6·95	5·74	0·14
Crude naphthalene	nil	nil	112 lb.	130 lb.	152·1 lb.	88·0 lb.
Crude anthracene	nil	nil	nil	nil	21·9 lb.	28·0 lb.
Creosote	56·0	77·40	34·3	20·9	42·34	23·0 lb.
Pitch	10·40 cwt.	9·72 cwt.	13·66 cwt.	14·57 cwt.	12·94 cwt.	15·64 cwt.

* A large part of the lower boiling oils of the Maclaurin tar were not condensed in the tar main and thus an apparently heavier tar results.

about 2 per cent. to over 16 per cent., and the sp. gr. from 1·133 to 1·214.[1] It contains much less light oil and middle oils than gas tar and more anthracene oils, yielding a rather greater quantity of pitch.

Schmitz [2] gives the following analyses of coke-oven tars from various sources :—

	1.	2.	3.	4.	5.	6.	7.	8.
Specific gravity	1·16	1·145 to 1·191	1·17	1·1198	...	...	...	...
Water	2·0	2·69	2·3	trace	6·60	3·20	3·40	3·70
Light oil	1·5	1·38	3·7	6·5	2·30	0·80	4·10	3·20
Middle oil	7·0	3·46	9·8	10·5	10·20	5·00	10·70	10·50
Heavy oil	14·0	9·93	12·0	7·6	8·00	8·40	8·60	7·40
Anthracene oil	14·0	24·76	4·3	44·3	26·70	22·70	19·00	16·8
Pitch	60·0	56·44	67·0	30·5	45·19	58·60	55·40	57·20
Loss	1·5	1·34	0·9	0·4	0·28	1·30	1·60	0·20

Weiss and Downs [3] from a detailed examination of large quantities of representative coke-oven tars give the average constituents as follows :—

	Per cent. by weight on dry tar.
Light oil :	
Crude benzene and toluene	0·3
Coumarone, indene, etc.	0·6
Xylenes, cumenes, and isomers	1·1
Middle and heavy oils :	
Naphthalene	10·9
Unidentified oils in range of naphthalene and methyl naphthalenes	1·7
α-monomethylnaphthalene	1·0
β-monomethylnaphthalene	1·5
Dimethylnaphthalenes	3·4
Acenaphthene	1·4
Unidentified oil in the range of acenaphthene	1·0
Fluorene	1·6
Unidentified oil in the range of fluorene	1·2
Anthracene oil :	
Phenanthrene	4·0
Anthracene	1·1
Carbazole and kindred nonbasic nitrogen-containing bodies	2·3
Unidentified oils, anthracene range	5·4
Phenol	0·7

[1] Prevost Hubbard, U.S. Dept. of Agriculture, Circ. 97, Washington, D.C., 1912.

[2] *Die Flüssige Brennstoffe*, Berlin, 1919, p. 59.

[3] *Ind. Eng. Chem.*, 1923, 15, 1022.

	Per cent. by weight on dry tar.
Phenol homologues (largely cresols and xylenols)	1·5
Tar bases (mostly pyridine, picolines, lutidines, quinolines, and acridine)	2·3
Yellow solids of pitch oils	0·6
Pitch greases	6·4
Resinous bodies	5·3
Pitch (melting point, 460° F.)	44·7
	100·0

The following table, due to Fisher and Morrell,[1] gives typical results for liquid-phase cracking (Dubbs process) of coke-oven tar, creosote oil and water-gas tar at a temperature of about 482° and a pressure of 200 lb. per sq. in.

	High-temperature coke-oven tar.	High-temperature creosote.	Water-gas tar.	
Specific gravity, 60°/60° F.	1·177	1·092	1·10	
Water	4·3	...	2·5	
Distillation (°C.) 10 per cent.	210	215	225	
Distillation (°C.) 50 per cent.	371	292	315	
Distillation (°C.) 90 per cent.	...	385	...	
End-point (°C.)	392	405	393	
Yield of motor spirit, per cent. by weight	13·1	4·3	14·4	25·2
Specific gravity, 60°/60° F.	0·785	0·831	0·761	...
Residuum	...	79·0	78·5	...
Pitch	61·2	...	...	...
Gas and loss	17·6	16·7	7·1	7·6
Coke	...	...	...	64·0

Further data on coke-oven tars are given by Spilker,[2] Watson Smith,[3] Chambers,[4] Childs,[5] and Adam.[6]

(f) Blast-Furnace Tar

This tar is only produced when blast furnaces work with coal, as for example in the West of Scotland where non-coking " splint " coals are occasionally employed. Approximately 7 gals. of tar are obtained per ton of coal. It is a light mobile tar with a sp. gr. generally slightly in excess of unity, and owing to the high oxygen content of the coal, the tar contains a high percentage of tar acids. Aromatic hydro-

[1] *J. Soc. Chem. Ind.*, 1933, **52**, 228 T; *cf.* Jones (W. H.), *J. Inst. Fuel*, 1930, **3**, 376.
[2] *Kokerei und Teerprodukte*, Halle (Saale), 1908.
[3] *J. Soc. Chem. Ind.*, 1883, **2**, 495.
[4] *J. Soc. Chem. Ind.*, 1922, **41**, 178 T.
[5] *Amer. Iron and Steel Inst.*, New York, 26th May 1916.
[6] *Trans. World Power Conf.*, 1924, **2**, 853.

carbons are present in small amount and the quantities of paraffins are considerable. The pitch content is low, but although bright and hard, it contains a high percentage of ash (5 to 30 per cent.), and a free-carbon content of 15 to 25 per cent. In common with the distillates from many low-temperature tars, all the fractions darken considerably in colour on standing. Naphthalene and anthracene are only present in small amounts.

A sample of Scotch blast-furnace tar examined by Watson Smith [1] had the following composition :—

Specific gravity of tar.	0·954.		
	Per cent. by volume.	Per cent. by weight.	Specific gravity.
Water	30·60	32·3	1·007
Oil up to 230°	2·91	2·8	0·890
Oil, 230° to 300°	6·97	7·1	0·971
Oil from 300° until oils solidify	13·02	13·5	0·994
Oils solidifying on cooling (soft paraffin scale)	16·75	17·3	0·987
Coke	...	21·5	...
Loss	...	5·5	...

Hooper [2] and Abraham [3] give the following figures respectively :—

I.		II.	
Specific gravity	0·954	Specific gravity	1·151
Distillate to 230°	2·9 per cent.	Mineral matter in tar	13·0 per cent.
,, ,, 300°	6·97 ,,	Water in tar	0·2 ,,
,, ,, 350°	33·0 ,,	Phenols in tar	14·6 ,,
Pitch	55 to 60 per cent.	Bases in tar	2·5 ,,
		Distillate up to 315°	43·4 ,,
		Pitch at 315°	56·6 ,,

The pitch is stated to be of medium hardness, paraffinoid in character, and unsuitable for briquetting purposes.

Edwards,[4] from a detailed examination of blast-furnace tar, obtained the following data :—

Nature of tar	Viscous, opaque and contained solid matter in suspension.
Specific gravity at 15°/15°	1·151
Nature of associated liquor	Alkaline.
Gases evolved during distillation	Ammonia, traces of hydrogen sulphide, and hydrocyanic acid in later stages.

[1] *J. Soc. Chem. Ind.*, 1883, **2**, 495 ; *J. Chem. Soc.*, 1886, **49**, 17.
[2] *J. Soc. Chem. Ind.*, 1910, **29**, 1438.
[3] Abraham, *Asphalts and Allied Substances*, London, 1938, p. 348.
[4] *J. Soc. Chem. Ind.*, 1924, **43**, 145 T.

Distillation.

Specific gravity of distillate . .	0·980
Water by volume	0·2 per cent.
Pitch at 311° by volume . .	56·9 ,,
Phenols on distillate by volume .	34·3 ,,
Phenols on tar by volume . .	14·6 ,,
Bases on distillate, weight/volume	5·8 ,,
Bases on tar, weight/volume .	2·5 ,,
Character of pitch	Paraffinoid, medium hard.

(*g*) Producer Tar

Producer tars are of low sp. gr., averaging 1·03 to 1·10. Low-temperature producer tars are similar in composition to low-temperature tars obtained by carbonization (p. 92) in that they contain naphthenes, relatively large quantities of tar acids, viscous oils, and solid paraffins. Depending on the type and operation of the producer, the tar may be either very mobile or almost solid, the latter being emulsified with large quantities of water which separates with difficulty. The gasification of coal in English low-temperature producers gives as much as 80 per cent. of the tar yield indicated by a laboratory low-temperature assay of the coal.[1] In general, however, the tar yield varies from nil to about 8 per cent. of the fuel. Excessive moisture in the fuel, high top temperatures in the producer, and rapid heating of the charge in its initial stages decrease tar yields, while an increase in the quantity of steam admitted to the producer increases the yield.

Calorific values of a producer tar and the fractions obtained therefrom are given below [2] :—

	Cals. per kg.	B.Th.U. per lb.
Calorific value of dry tar	8500	15,300
,, ,, ,, lightest tar-oil fractions	9600	17,300
,, ,, ,, heaviest tar-oil fractions	8400	15,100
,, ,, ,, tar acids in oil fractions	7800	14,000

Producer tars vary in composition according to the character of the fuel and the nature and operation of the plant. Producer plants and the varieties of tars obtained therefrom are discussed extensively by Rambush,[3] from whose publication the following tables are quoted.

[1] Rambush, *Modern Gas Producers*, London, 1923.
[2] Fischer and Gluud, *Abh. z. Kennt. der Kohle*, Part I., 1916.
[3] *Modern Gas Producers*, London, 1923, p. 112.

Fractional Distillation and Tar Yields

	A.	B.	C.	D.		E.	
	Ordinary producer. Indian coal. 25 per cent. volatile matter. Low load factor.	By-product recovery plant, Lymm type. American coal. 30 per cent. volatile matter.	Mond gas plant. Scotland. Coal, 37 per cent. volatile matter.	Nottinghamshire slack. 36 per cent. volatile matter.		Yorkshire nuts. 34 per cent. volatile matter.	
				1. Mond gas tar.	2. Semi low-temperature producer tar.	1. Semi low-temperature producer tar.	2. Low-temperature producer tar.
Per cent. dry tar yield on dry coal	...	...	3·6	2·08	5·2	7·6	9·5
Per cent. moisture in undehydrated tar	27·2	24·0	38·0	10·0	2·0	33·0	50·0
Distillates per cent. by weight on dry tar:—							
70° to 170°			0·7	0·5	1·0	1·5	1·0
170° „ 230°	18·2	4·9	3·3	3·3	6·8	7·8	10·5
230° „ 270°			6·9	...	10·7	12·6	10·3
270° „ 300°	17·5	22·4	7·2	10·5	24·6	7·0	9·6
300° „ 350°			14·1			13·7	31·7
Above 350°	...	...	26·1	...	14·9	17·3	12·8
Residue and loss	64·3	73·7	37·0	75·7	41·6	37·5	24·2

(*h*) Water-Gas Tar

Water-gas tar is generally of an oily consistency and brown in colour. It often contains as much as 85 per cent. of practically ammonia-free water; the greater the percentage of water the more viscous is the resulting emulsion.[1] Separation of the water by ordinary means is difficult. Weiss[2] states that the free-carbon varies from 1·04 to 1·087 per cent., with tars ranging in specific gravity from 1·078 to 1·090. Tar bases, phenols, and carbazole are generally present only in small quantities. Swolobov[3] reports that an anhydrous water-gas tar contained, per cent., benzene, 0·7; toluene, 0·03; crude naphthalene, 8·0; anthracene, 1·1; phenanthrene, 2·0; and acenaphthene, 0·8; the crystalline products, containing 50 per cent. of crude naphthalene, amounted to 16 per cent. Styrene has been identified in two samples of water-gas tar, being present to the extent of 0·7 and 0·9 per cent. of the volume of the tar respectively in the oils distilling

[1] Odell, Technical Paper No. 304, Bureau of Mines, Dept. of Interior, Washington D.C., 1923.

[2] *J. Franklin Inst.*, 1911, **172**, 277.

[3] *J. Chem. Ind. Russ.*, 1929, **6**, 206.

between 130° and 160°, and indene to the extent of 1·9 and 1·2 per cent. respectively in the 160° to 190° fraction.[1]

German Gas Producer Tar Yields and Composition

Fuel.	Saar coal.		Upper Silesian coal.		Lausitz screened run-of-mine.		Brown coal briquettes.	
Type of gas producer.	1. Low-temperature gasification.	2. Linck's mechanical retort.	1. Low-temperature Mond gas producer.	2. Low-temperature gasification.	1. Mechanical grate producer with distillation chambers.	2. Heller gas producer.	1. Heller gas producer.	2. Generator of A.G.B.
Per cent. tar yield	5 to 5·5	6	6 to 7	6 to 6·5	2 to 2·3	none	?	10 to 12
Tar properties: Specific gravity (15°)	1·104		1·059	1·02 to 1·05	1·012	...	1·005	0·98
Per cent. mechanical impurities	2·36		2·03	1·3	0·52	...	0·58	0·4 to 0·5
Viscosity at 100°	...		1·69	1·7	...	...	1·84	...
Per cent. oil yield	59·5		66	72	66	...	68·7	70
Per cent. pitch yield	39·7		33	27	32	...	30	28
Properties of tar oil: Specific gravity (15°)	1·020		1·022	1·023	1·008	...	...	0·97
Viscosity at 50°	1·41		2·0	1·8	2·5	...	...	2·5
Ignition temperature °C.	108		105	96	112	...	...	105
Solidification temperature	−2°		−2°	−1°	...	...	...	18°
Per cent. paraffin	1·95		2·8	2·92	3·5	...	11·8	10 to 14
Melting point of paraffin	58		51	52	51	...	51·5	50·5
Per cent. tar acids	40		36	37	26	...	13	28
Per cent. asphalt	3·07		...	...	8·9	...	...	...
Oil fractions after removal of paraffins in per cent. on tar								
Light oils, per cent.	25·5		27	30	...	...	26·5	24·0
Specific gravity (15°)	0·976		...	...	...	...	0·97	0·94
Ignition temperature	89°		82°	85°	..	...	95°	95°
Per cent. lubricating oils	31·4		37	30	...	...	35·5	44
Ignition temperature	148°		152°	150°	...	...	179°	150°
Viscosity at 50°	4·97		4·9	6 to 7	...	...	8·5	4 to 5
Properties of pitch: Twisting point	100°		76° to 77°	83° to 84°	92·5°	...	57·5°	65°
Per cent. insoluble in benzole	22·7		12·3	16·7	12·8	...	traces	15
Per cent. ash	1·11		0·72	1·09	0·46	...	...	0·6

Mathews and Goulden[2] determined the composition of a tar obtained from water-gas carburetted with crude Russian petroleum, with the following result :—

[1] Brown and Howard, *Ind. Eng. Chem.*, 1923, 15, 1147.
[2] *Wagner's Jahresber.*, 1892, p. 77.

	Per cent.
Benzene	1·19
Toluene	3·83
Light paraffins	8·51
Solvent naphtha	17·96
Phenols	traces
Middle oil	29·44
Heavy oil	24·26
Naphthalene	1·28
Crude anthracene	0·93
Coke	9·80
	97·20

Glover [1] discusses in considerable detail the influence of temperature on the composition of carburetted water-gas tar. The following data are abstracted from his paper :

Typical analysis of gas oil employed

	Per cent.
Olefines	17
Aromatics	3
Paraffins and naphthenes	80
Polycyclic compounds	slight traces
Specific gravity	0·870

	1.	2.	3.	4.	5.
Temperature °C.					
At base of superheater	720	740	770	800	820
Below oil injectors	715	730	755	780	800
At top of superheater	710	730	760	780	805
Gas oil used per minute (gals.)	6·14	6·14	6·14	5·60	5·44
Specific gravity of tar	1·060	1·087	1·095	1·090	1·120
Total polycyclic compounds calculated as naphthalene	14·7	16·1	18·9	21·0	23·0

Analysis of tar oil fractions (0° to 300°)

	Per cent. olefines.	Per cent. aromatics.	Per cent. paraffins and naphthenes.
1	36·0	22·0	42·0
2	57·0	28·0	15·0
3	65·0	32·7	2·3
4	69·5	29·1	1·4
5	34·0	60·0	nil

[1] *Gas J.*, 1930, **191**, 702 ; 1930, **192**, 38.

The results obtained using gas oil, light and heavy creosote, and mixtures of gas oil and creosote as cracking stock in an atmosphere of hydrogen and carbon monoxide are indicated by the following typical results [1] :—

Nature of oil.	Therms as oil gas per gal. of oil.	Tar, per cent. by weight of oil.	Naphthalene in tar, per cent. by weight of oil.
Gas oil	1·211	30·1	3·0
Light creosote (from steamed vertical retorts)	0·489	67·7	16·0
Heavy creosote (from horizontal retorts)	0·167	80·3	18·3
Mixture of 80 per cent. gas oil and 20 per cent. light creosote, by volume	1·054	40·1	6·3

Analyses of the gas oil used on a back-run Humphreys and Glasgow water-gas plant, and of the tar recovered, are given below [2] :—

Gas Oil.

Ultimate Analysis :	Per cent.
Carbon	86·9
Hydrogen	12·7
Sulphur	0·3
Ash	0·0
Nitrogen and oxygen (difference) .	0·1
	100·0

Constituents of Oil.

	Per cent. by volume.
Paraffin hydrocarbons .	53·3
Unsaturated hydrocarbons .	5·4
Aromatic hydrocarbons .	22·1
Naphthenic hydrocarbons .	16·6
Residue above 380° C. .	2·6
	100·0

Specific gravity of oil at 15·5° C. . . . . . 0·855
Calorific value (gross), B.Th.U. per lb. 19,640

Tar Recovered.

Ultimate analysis :	Per cent.
Carbon	90·5
Hydrogen	7·2
Sulphur	0·7
Ash	0·0
Nitrogen and oxygen (difference) .	1·6
	100·0

Distillation of Dehydrated Tar.

First drop . . . 110°

Fractions.	Per cent. by volume.
Below 170°	1·5
170° to 230°	13·5
230° ,, 270°	34·3
270° ,, 350°	26·2
Pitch (by difference) . .	24·5
	100·0

Specific gravity of tar at 15·5° . . . . . 1·040
Calorific value (gross), B.Th.U. per lb. 17,760

[1] Cobb, General Introduction, 25th, 26th, 27th Reports, Joint Research Committee, Inst. Gas Engs., *Gas J.*, 1930, **192**, 702.

[2] Twenty-seventh Report, Joint Research Committee, Inst. Gas Engineers and Leeds University, *Gas J.*, 1930, **192**, 704.

Additional data are given by Abraham [1] of the general properties of water-gas tars, from which the following are selected :—

Viscosity at 212° F. (100 ml.)	25 to 50
Fixed-carbon	10 ,, 20 per cent.

Distillation :	Per cent. by weight.	Specific gravity.
Naphtha (up to 110°)	0 to 5	0·85 to 0·90
Light oils (110° to 170°)	0·5 ,, 5·0	0·88 ,, 0·90
Middle oils (170° to 235°)	5 ,, 35	0·98 ,, 1·00
Heavy oils (235° to 270°)	7 ,, 30	1·00 ,, 1·07
Anthracene oil (270° to 350°)	10 ,, 25	1·07 ,, 1·10
Water-gas tar pitch (residue)	20 ,, 70	...

Solubility in carbon disulphide	95 to 100 per cent.
Solubility in 88° petroleum naphtha	20 ,, 75 per cent.
Naphthalene	Less than 10 per cent.
Solid paraffins	Nil to 5 per cent.

The yield of products obtained by cracking water-gas tar is given on p. 112.

(*l*) Oil-Gas Tar

Oil-gas tar is black in colour, of low sp. gr. (0·95 to 1·10 at 77° F.), and distinguished from coal tar by the almost entire absence of phenolic and basic substances and of thiophen and its homologues. The free-carbon content rarely exceeds 22 per cent., but varies according to the degree of cracking of the oil used. Abraham [1] states that oil-gas tars may contain from nil to 5 per cent. of solid paraffins, and a trace of naphthalene. Benzene, toluene, xylene, naphthalene, acenaphthene, anthracene, phenanthrene, chrysene, and presumably pyrene, were identified by Zanetti and Egloff [2] in the oil tar obtained from a natural gas condensate. Wurth [3] found the following constituents in an oil-gas tar prepared in the brown coal industry in Saxony and Thuringia :—

Constituent.	Per cent.	Constituent.	Per cent.
Benzene	1·00	Naphthalene	4·90
Toluene	2·00	Crude anthracene	0·58
Xylene	1·30	Phenols	0·30
Resinifiable oils below 150°	1·00	Bases	traces
Oils from 150° to 200°	1·50	Asphalt	22·00
Oils from 200° ,, 300°	26·60	Free-carbon	20·50
Oils from 300° ,, 360°	12·60	Water (neutral)	4·00

Most of the characteristic constituents of coal tar, with the exception of carbon disulphide and acridine, could be detected in this oil-gas tar.

[1] Abraham, *Asphalts and Allied Substances*, London, 1938, p. 381.
[2] *Ind. Eng. Chem.*, 1917, **9**, 474. [3] *Dissertation*, Munich, 1904.

Distillation analyses of a variety of oil-gas tars are given below :-

	Brown coal industry.*	Natural gas condensate.†		Gas oil ‡ (Dayton process).		
Distillation range.	Per cent.	Distillation range.	Per cent.	Distillation range.	Per cent.	
					(a)	(b)
First runnings from 70° to				Up to 80°	none	none
110° and 150° . . .	5 to 10	To 170°	9·7	80° to 170°	13·8	10·2
Light oil from 150° to 200°.	5 to 10	170° to 230°	18·7	170° „ 230°	26·8	26·8
		230° „ 270°	11·4	230° „ 270°	15·2	18·4
Middle oil from 200° to 250°	20	270° „ 330°	15·1	270° „ 360°	32·6	31·0
Heavy oil from 250° to 300°	20	Over 360°	...	Pitch	11·3	12·7
		Residue	30·1	Water	0·6	0·6
Anthracene oil over 300° .	30	...	...	...	...	...
Pitch and loss . . .	10	...	...	Loss	0·7	0·7
				First drop	85°	83°
Specific gravity of tar . .	...		1·109		0·986	0·988

* Scheithauer, *Fabrikation der Mineralöle*, p. 316.
† Zanetti and Egloff, *Ind. Eng. Chem.*, 1917, **9**, 474.
‡ Binnall, *Ind. Eng. Chem.*, 1921, **13**, 242.

Light spirit was recovered from the oil gas from tar No. 3 above, the fractions of which after acid and alkali washing amounted to :—

	(a) Per cent.	(b) Per cent.
Light naphtha up to 80°	14·0	9·8
Purified benzene, 80° to 100°	26·0	43·7
Purified toluene, 100° to 120°	12·7	15·8
Purified xylene, 120° to 145°	12·7	1·6
Solvent naphtha, 145° to 170°	8·8	7·5
Residue above 170°	4·4	1·4
Removed by sulphuric acid	21·4	20·2
Paraffins in fraction, 80° to 145°	none	none

Letny [1] gives the following analysis of an oil-gas tar prepared by passing heavy petroleum tailings through red-hot tubes to convert them into aromatic hydrocarbons :—

	Per cent.	
Water	2·3	
Light oil up to 90°	4·6	Benzene, toluene, xylene, etc.
Light oil from 90° to 140°	5·2	
Middle oil from 140° to 200°	1·8	
Heavy oil from 200° to 270°	26·9	Naphthalene and unaltered petroleum.
Anthracene oil from 270° to 340° . . .	8·6	
Anthracene oil above 340°	27·5	Anthracene and phenanthrene.
Pitch	20·6	
Loss	2·5	

[1] *Dingl. polyt. J.*, 1878, **229**, 353.

The sp. gr. of this tar (1·207) was remarkably high. In general, the yield of oil-gas tar increases with the rate of the oil feed at a given temperature, and with a decrease in temperature at constant rates of oil feed. At slow rates of oil feed at high temperatures no tars are produced.[1]

(*j*) Bergius Tar

Hydrogenation of coal at pressures in general up to 200 atm. and above, and at temperatures ranging from 300° to 500°, yields varying amounts of tar of a composition dependent on the character of the coal and the conditions of hydrogenation. The higher the temperature, within the above limits, and the greater the pressure, the larger the proportion of light products. The presence of catalysts, the use of a large variety of which has been the subject of numerous patents, also modifies the yield and character of the resulting tar or oil. Tars produced by the hydrogenation of coal are usually of a viscous nature and dark in colour, and as recovered from the plant contain water and solid matter in suspension. The solid matter, which may amount to as much as 30 per cent., is often difficult to remove either by filtration or centrifuging, while complete settling is long delayed. If not removed, distillation of the product is slow and frothing is excessive, and the resultant pitch contains too high a proportion of solid inorganic material to be a good binder.[2] Bowen, Shatwell and Nash [3] state that tars obtained in small-scale experiments were completely soluble in chloroform, but deposited brown amorphous powders on treatment with ether, benzene, light petroleum and carbon tetrachloride producing strongly fluorescent solutions. Alcohol exerted only a slight solvent action. Ultimate analyses of typical neutral oils from these tars are given below :—

	Carbon.	Hydrogen.	Sulphur.	Nitrogen.	Oxygen.	Ratio : $\frac{\text{carbon}}{\text{hydrogen}}$
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	
Clarain tar *	85·98	7·59	0·01	1·12	5·30	11·3
Durain tar *	86·20	7·73	0·01	1·20	4·86	11·1
Graigola tar *	87·30	7·60	0·58	0·89	3·63	11·5
Arley tar †	87·08	7·06	0·40	1·68	3·78	12·3
Cellulose tar	88·41	7·94	nil	nil	3·64	11·1

* *Fuel*, 1925, 4, 130. † *Ibid.*, p. 254.

Bergius [4] claims a yield of 107 to 185 gals. of tar per short ton of coal as mined. From 1000 kg. of coal he obtained gasoline, 150 kg. ;

[1] Whitaker and Alexander, *Ind. Eng. Chem.*, 1915, 7, 484.
[2] King, *J. Soc. Chem. Ind.*, 1927, 46, 181 T.
[3] *J. Soc. Chem. Ind.*, 1925, 44, 507 T.
[4] Pittsburg Conference, *Min. J.*, 1926, p. 1013.

middle fraction, 200 kg.; fuel oil, 80 kg.; and lubricating oil, 60 kg., a total of 49 per cent. of the coal used. Heyn and Dunkel [1] give a yield of 44·3 per cent. on hydrogenating a Silesian coal dust, of which 3·4 per cent. was light spirit. The tar had the following composition :—

	Per cent.	
Neutral oil	75·7	(polymethylenes, aliphatic compounds, and substituted aromatic compounds).
Phenols	12·0	(chiefly phenol with smaller quantities of cresols and xylenols).
Bases	3·5	(aniline, toluidine, xylidine, collidine, quinoline, quinaldine, but no pyridine).
Resin	1·1	
Residue	0·5	
Loss	7·2	

The gas spirit contained benzene, toluene, xylene and hexahydro-derivatives. The fraction boiling from 180° to 220° contained naphthalene, and tetra- and deca-hydro-derivatives. The neutral oil contained 0·7 to 1·1 per cent. of sulphur.

British coals tested on a 1-ton per day plant at Rheinau yielded 50 to 60 per cent. of the coal as crude tar and spirit. Analyses of typical products are given by the Fuel Research Board [2] in the following table.

When low temperatures and small quantities of hydrogen (1 per cent.) are employed, pitch-like products are formed.[3] Light spirits are also obtained, both from the gas produced and the tar. Low-temperature and high-temperature tars and their products have also been hydrogenated for the production of further quantities of light-boiling spirit.[4]

A variation of the process to allow of recovery of oil from a circulating stream of hydrogen results in the recovery of an oil essentially different from those described previously. The oil is dark red brown in colour, perfectly clear and transparent in thin layers, and on distillation to 360° does not yield a pitch but a thick, heavy, waxy oil. The original oil is free from solid matter. As hydrogenation proceeds, the proportion of oils boiling below 230° diminishes and that boiling above 360° rapidly increases, while the quantity of phenols appears to decrease and the neutral oil to increase. The heavy fractions on rehydrogenation lose all resemblance to tar. Skinner [5] gives an extensive bibliography of technical and patent literature bearing on coal hydrogenation. Detailed experimental

[1] *Brennstoff-Chem.*, 1926, **7**, 20, 81, 245. [2] *Ann. Report*, 1930.
[3] B.P. 301720/1930. [4] *J. Inst. Fuel*, 1932, **6**, 33. [5] *Fuel*, 1931, **10**, 109.

work on coal hydrogenation and the products so obtained is described in the Annual Reports of the Fuel Research Board from 1933 to 1937.

Temperature of hydrogenation °C.	450 to 480.		445.*		455.*	
Name of coal	Parkgate seam.		Virgin seam (Lancs.).		Virgin seam (Lancs.).	
	1.		2.		3.	
Yield of oil.	Lbs. per ton of coal.	Per cent. weight of coal.	Lbs. per ton of coal.	Per cent. weight of coal.	Lbs. per ton of coal.	Per cent. weight of coal.
Fraction °C.						
0 to 170	83	3·7	42	1·9	48	2·1
170 „ 230	208	9·3	187	8·3	164	7·3
230 „ 270	197	8·8	131	5·8	144	6·4
270 „ 310	105	4·7	105	4·7	116	5·2
310 „ 360	208	9·3	150	6·7	136	6·1
Pitch	329	14·7	629	28·1	683	30·5
Gas spirit	42	1·9	16	0·7	18	0·8
Total	1172	52·4	1260	56·2	1309	58·4

Composition of oils distilling below 360° and excluding light spirit.	1. Per cent.	2. Per cent.	3. Per cent.
Unsaturated and aromatic hydrocarbons	62·4	57·2	55·2
Saturated hydrocarbons	14·6	8·6	13·3
Phenols	17·0	17·9	22·7
Bases	6·0	6·4	7·0
Loss (carboxylic acids, etc.)	...	9·9	1·8
Total	100·0	100·0	100·0

* Catalysts employed.

III. STANDARDIZATION OF TESTS

Standard Methods for Testing Tar and its Products [1] was first published in England in 1929 by a standardization committee representative of the chief scientific and industrial bodies interested in the production and utilization of coal tar and coal-tar products. The committee thoroughly revised and considerably extended the British standard tests, issuing the second edition late in 1938. These Standard Methods have been widely accepted and rapidly replaced those more empirical ones formerly in general use in the industries. Certain of the methods have been incorporated in specifications issued by the British Standards Institution, the British Road Tar Association,

[1] Published by the Standardization of Tar Products Tests Committee, London, 1938.

and the National Benzole Association, while overseas many of the Standard Methods have been adopted as they stand or with little material alteration. In Germany, standardization has been concerned mainly with road tars, asphalts and roofing preparations, standard tests being described in specifications issued by the Deutscher Normenausschuss. Specifications for commercial benzoles published by the Benzolverband are also widely known and adopted. In France, standardization is similarly limited to a few coal-tar products, notably road tar, benzoles and pitch. In America, although there appears to be no complete correlation or unification of methods of testing, many methods may be considered to be standardized by tacit agreement between large industrial organizations and national bodies of the character of the American Society for Testing Materials. A *Book of Standards* is published triennially by the last-named body, supplementary tests being issued in pamphlet form as required within the triennial period ; a new edition of the American Society for Testing Materials Standards was issued in 1936. Coal tar and coal-tar products receive treatment in Part II. of this publication. Methods for the testing of creosote oil are uniform as regards the American Wood Preservers' Association, the American Railway Engineering Association, and the American Society for Testing Materials, but numerous specifications are issued by other organizations. The International Advisory Office on Wood Preservation, an organization of the principal creosote oil-producing countries of Europe, has in recent years issued specifications and methods of test for creosote oil for use in timber preservation.[1, 2] The methods of testing tar and tar products [3] adopted by the Barrett Company, many of which are substantially those described by the American Society for Testing Materials, have been received with respect and adopted to a considerable extent by others connected with the coal-tar industries. Hereinafter " Standard Method " refers specifically to the method described in the British publication, *Standard Methods for Testing Tar and its Products*, 2nd edition, 1938. The Standard Methods have been carefully summarized in the following pages, but it will be appreciated that the original publication must be consulted when a determination purporting to be carried out by the Standard Method is in hand.

[1] *Scandinavian Specification and Methods of Test for Coal Tar Creosote Oil as used for the Impregnation of Wood,* International Advisory Office on Wood Preservation, The Hague, 1937.

[2] *Budapest Specification and Methods of Test for Coal Tar Creosote Oil as used for the Impregnation of Wood, ibid.*, 1938.

[3] *Methods of Testing Coal Tar Products,* The Barrett Company, New York, 1931.

IV. THE SAMPLING OF COAL TAR AND ITS PRODUCTS

The Standard Methods for the sampling of coal tar and its products [1] have been adopted by the British Standards Institution [2]; the provisions therein are summarized below. No specification, however explicit, can take the place of judgment, skill and experience in sampling, and the standards which have been laid down are intended to serve as a supplement to such experience and as a guide in the selection of the best method in any particular circumstances.

Every precaution must be taken and a reliable method adopted to ensure that the sample *shall be and remain truly representative* of the bulk of the material which is to be tested. The sampling apparatus must be clean and the sampling procedure such as to preclude contamination of the bulk material and the sample taken. Great care must be exercised to guard against loss of the more volatile constituents by undue exposure. Products which are affected by exposure to light should be stored in metal vessels or in amber-coloured glass bottles. Rubber stoppers must not be used for closing the containers. If sealing-wax or pitchy composition is used for sealing purposes, this must be employed in such a way that when the vessels are opened the contents are not contaminated by the material of the seal. Refined materials must be protected by covers of oil-proof paper, metal foil or analogous impervious material over the stopper and top to keep moisture and dust away from the mouth of the vessel and to protect it while being handled. Such covers also prevent sealing substances from getting on the lip when the seal is made or later opened, and so contaminating the sample when it is poured out.

FIG. 21.—Closable Sampling Tube.

In the sampling of liquids it may be convenient to use an open tube made of metal or glass, and of such a bore that when immersed, the upper end can be sealed with the thumb. The contained liquid is withdrawn from the bulk and discharged into the sample vessel. The

[1] *Standard Methods for Testing Tar and its Products*, 1938, pp. 13-30.

[2] Extracted by permission from *B.S.* 616, 1938: "Sampling of Coal Tar and its Products."

tube must be wiped externally to prevent any adherent liquid passing into the sampling vessel.

Fig. 21 shows the construction of a useful type of metal sampling tube. Operation of the small lever at the top of the tube opens or closes the opposite end. The valve should be so arranged to allow of a sample being obtained from the extreme top to the extreme bottom of the liquid. When tubes are used they should be immersed slowly, so that the level of the liquid in the sampling tube is the same as that outside the tube.

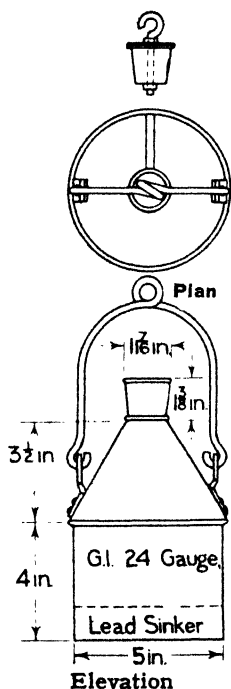



FIG. 22.—Sampling Can.

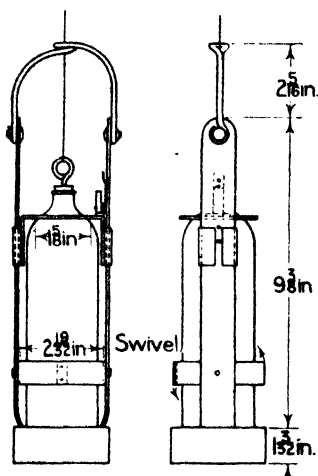



FIG. 23.—Sampling Case with Removable Bottle.

A small metal bottle, weighted with a lead sinker and provided with a tightly-fitting stopper to which a long string is attached, may be employed instead of a tube. Figs. 22 and 23 show the form and dimensions of suitable sampling bottles. The bottle is lowered to a predetermined depth in the liquid, the stopper removed by pulling on the string, and the bottle allowed to fill. For sampling solids such as naphthalene and anthracene, a sampling scoop is desirable (Fig. 24). To agitate a liquid prior to or during sampling, a metal disc about 18 in. in diameter, perforated with a number of 1-in. holes and fixed centrally to a metal rod or pipe, is suitable. Air should not be used for agitation, since its indiscriminate use may be dangerous or result in oxidation or contamination of the material.

The sampling of heterogeneous liquids in transit through pipe lines by tapping the line may give unrepresentative samples and should not be adopted if other methods are available. Whenever practicable, heterogeneous liquids should be sampled at the open end of the discharge pipe, using a ladle or can which is large enough to take the full stream for a short specified period at regular intervals during the whole period of discharge. If tapping of a pipe line is the only available method the sampling point should be in a rising section of the pipe line and on the discharge side of any pump in the system. A sampling pipe should extend internally one-third of the diameter of the pipe line, the inner end being bent at 90° to face the stream of liquid. The pipe should be fitted with a plug-cock adjusted to give a steady continuous flow of oil over the whole period of discharge of the liquid. An alternative arrangement is shown in Fig. 25; in use, the three cocks are opened to an equal extent, the amount of opening being such that about 0·1 per cent. of the stream is diverted. Various precautions for the taking and subsequent manipulation of the tapped material must be taken, and a simplified form of the arrangement in Fig. 25 is available. Weiss[1] recommends that the receiver be provided with a steam coil to keep the contents fluid, but the temperature must not exceed 120° F.

Fig. 24.—Sampling Scoop.

Sampling of liquid while at rest in tanks of uniform horizontal cross-section throughout their depth is best carried out with a tube sampler if the tank is not too deep; otherwise a sampling bottle must be used to withdraw portions of the liquid at equally spaced levels throughout. A divided suspension cord or chain, or the use of a calibrated rod, minimizes the possibility of error in determining the levels for can sampling.

When placed horizontally, cylindrical tanks should in general be sampled in accordance with Fig. 26 and the table on p. 124, samples of equal amount being taken, one at A, two at B, two at C, and one at D. If the tank is not approximately full, the procedure must be modified accordingly. A, B, C and D are the volume centres of the respective sections.

[1] *Ind. Eng. Chem.*, 1918, 10, 732.

Sampling of Cylindrical Tanks

Volume Centres.	Number of samples to be taken.	Depth of sampling positions.	
		Cylindrical vessels.	Vessels with hemispherical ends.
A	1	d.×0·14	d.×0·18
B	2	d.×0·37	d.×0·39
C	2	d.×0·63	d.×0·61
D	1	d.×0·86	d.×0·82

In the case of dish-ended vessels the sampling depths should be adjusted, from the proportion of the volume of the ends to the volume of

FIG. 25.—Continuous Sampling Connection.

the cylindrical portion ; *e.g.* in the case of a boiler 6 ft. in diameter, of which the volume of the ends together is equal to one-sixth of that

FIG. 26.—Sampling of Horizontal Cylindrical Tanks—Sampling Positions.

of the cylindrical portion, the samples at A and D should be taken about one-half inch lower and higher respectively.

Weiss[1] submits that in the sampling of tank cars samples should be taken from three zones, namely, the top-foot section, the middle-foot section, and the bottom-foot section, these being combined as shown below :—

Diameter of car, feet.	Zone.	Proportionate weight of sample.
6	Top.	11
	Middle.	25
	Bottom.	11
7	Top.	1
	Middle.	2
	Bottom.	1
8	Top.	1
	Middle.	3
	Bottom.	1

If possible, any free water should be drawn off, the quantity reported separately and, where necessary, sampled. When the tar or tar fraction is contained in casks or drums the quantity of subnatant aqueous liquor should be ascertained either by its withdrawal and direct measurement or by emptying the container into a measured tank and allowing time for gravity separation.

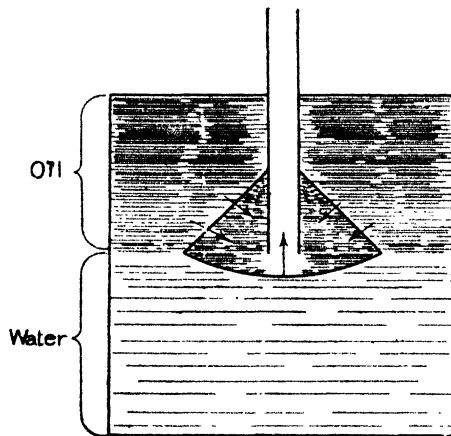



FIG. 27.—Take-off Pipe with Baffle.

Supernatant liquor can be measured only by the latter method. Alternatively, if such methods are not applicable, a strip of water-finding paper attached to a dipping rod may suffice to determine the amount of subnatant liquor. Fig. 27 shows a device which overcomes most of the usual difficulties in separating the contents of a tank holding

[1] *Loc. cit.*

two immiscible liquids which have settled to give a reasonably good line of demarcation between the constituent layers. The upper layer is withdrawn through the vertical tube by pumping, the baffle preventing the movement of the lower layer.

When tank cars are provided with sampling cocks the nipple should extend at least 6 in. inside the tank shell and the cock be opened for the nipple to clear well before the sample is taken. Samples from the sides of a tank should not be taken too close to the bottom of the tank. Tank car and tank barges which are compartmented should be sampled separately in each compartment; an inaccessible compartment may be sampled from the stream during discharge. Sampling of solids should, whenever possible, be done while the material is in transit, regular and frequent quantities being combined and mixed to form the gross sample, from which the laboratory sample may be obtained after reduction in size of the material and thorough mixing (*cf.* Vol. I., p. 5).

When products are received in casks, drums or sacks, every container should, if practicable, be separately sampled, but if this is inconvenient, the minimum number to be sampled should be in accordance with the following table or graph.

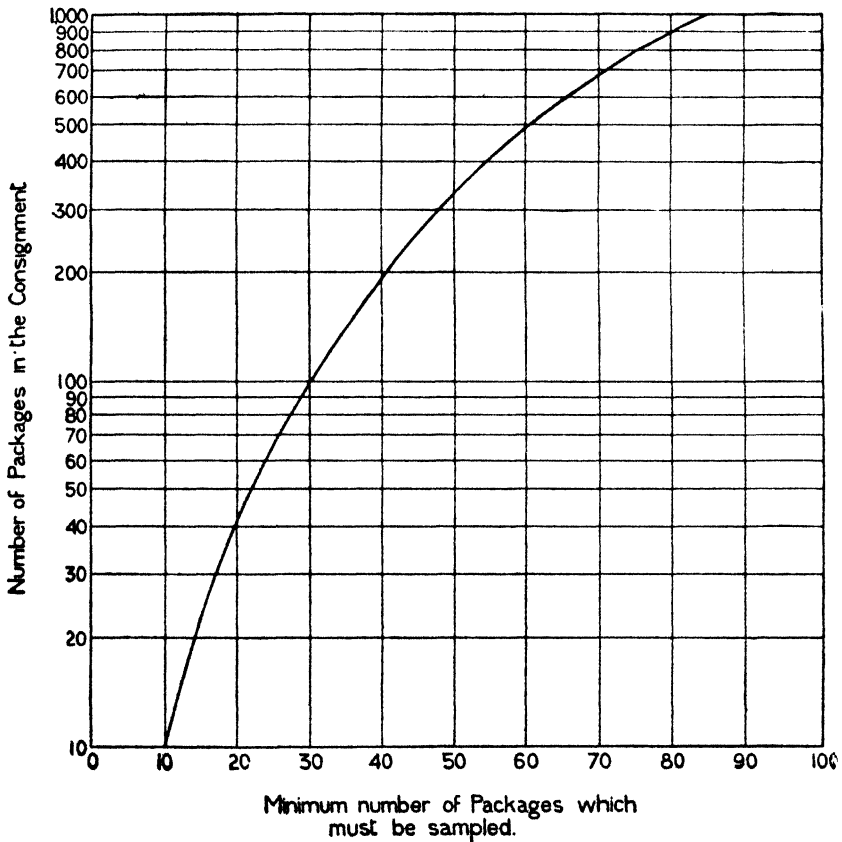
Samples taken from heaps or cars are, in general, not representative. If sampling has to be carried out under these conditions, small samples should be taken from at least twelve points throughout the bulk and collected to form the combined sample. Alternatively, two trenches at right angles to one another may be driven through the heap and the material so removed collected to form the bulk sample. (In sampling car loads, eight samples should be taken from the corners of the car, and four each near the top and bottom of the car. To these should be added four samples from the centre of the car and two each from the top and bottom centres of the car.)[1] In reducing the size of the sample the usual coning and quartering method should be employed, on a clean impervious surface. The following relationship between the weight of the bulk sample and the size of the largest pieces must be observed :—

Weight.	Maximum size of pieces.
Lb.	Inches.
50 and over.	1
25 to 50	$\frac{1}{2}$
5 to 25	$\frac{1}{4}$
Under 5	$\frac{1}{10}$

Samples of anthracene should finally be rubbed through a British Standard No. 18 test sieve and then thoroughly mixed. This may be

[1] Weiss, *loc. cit.*

Sampling of Packages.

Number of packages in consignment = N.	Minimum number of packages to be sampled.
1 to 10	Each one
11 ,, 20	10+(N− 10)/3
21 ,, 50	14+(N− 20)/4
51 ,, 100	22+(N− 50)/7
101 ,, 200	30+(N−100)/9
201 ,, 500	41+(N−200)/15
501 ,, 1000	61+(N−500)/22

GRAPH I.

impracticable with a particularly oily sample ; in such cases, the *bulk* sample must be passed through a standard $\frac{3}{16}$-in. test sieve and then reduced by quartering. The reduced sample is passed through a standard No. 8 test sieve or, if that is impracticable, it is passed a second time through the $\frac{3}{16}$-in. sieve.

Coning is facilitated by the use of a funnel supported vertically over the growing apex of the heap and raised periodically as the material is fed through it.

In sampling carbolic acid crystals a selected number of drums should be allowed to stand in an open tank or on a grid below which a closed steam coil is fitted. When the acid is completely melted a sample may be withdrawn with a glass tube after thorough agitation with a smooth hard wood stirrer. Care should be taken to minimize exposure to the atmosphere. The colour and condition of carbolic acid may be altered by heating or the absorption of small traces of water or by exposure to light. The sampling procedure for pitch has been elaborately discussed by the interests concerned. The following brief summary must therefore give place to the detailed technique of *Standard Methods* if actual sampling of a consignment is intended. In sampling pitch in bulk during conveyance, regular increments should be taken from the conveying plant at frequent intervals during loading or unloading. When the pitch is in barrels the upper 2 in. should be removed from the surface of the pitch in the selected barrels, and pieces of pitch of approximately equal size cut out, one from each barrel. The presence of any foreign matter should be noted. Pitch in store in pitch bays is best sampled by excavating one or more holes to expose a face the full depth of the pitch. Samples of equal size may then be taken from the face at equidistant points. The following is recommended :—

Depth of face.	Procedure.
1 ft.	Take one complete section of the face.
1 to 3 ft.	Take two separate samples.
3 to 6 ft.	Take three separate samples.
Over 6 ft.	Take four separate samples.

The pieces in a bulk sample must be trimmed to weigh about 8 oz. each and then placed on a clean hard surface where they are each broken down until the whole of the bulk sample will pass a standard $\frac{1}{4}$-in. test sieve. The bulk sample is reduced by quartering to provide the agreed number of samples, each of about 2 lb.

The above pitch sampling procedure takes no account of " dusty smalls " which are almost always present in a bulk consignment. Agreement between buyer and seller must be sought in the sampling of this material.

V. DETERMINATION OF DENSITY, SPECIFIC GRAVITY AND DISTILLATION RANGE—GENERAL NOTES

Certain general principles relating to the determination of density, sp. gr. and distillation range are laid down in *Standard Methods*; the discriminate application of these general principles is necessary in the testing of individual tars and tar fractions.

(*a*) **Density and Specific Gravity.**[1]—Apart from a lack of clarity in conception of the sp. gr. basis, there are various arguments for its replacement by density as the fundamental concept.[2] But the use of sp. gr. as a criterion in tar products testing is established and likely to be difficult to replace. In the circumstances, those concerned in the manufacture, sale and use of tar and tar products are gradually introducing density criteria, envisaging an ultimate replacement of the present customary sp. gr. basis.

The second edition of *Standard Methods* deals with both density and sp. gr. determinations.

(*b*) **Density.**—The adoption of 20° C. as the standard reference temperature for the calibration of volumetric glassware [3] has encouraged the use of that temperature as a basic one in other directions and the provisions for density tests in *Standard Methods* are based on determinations at 20° C., *i.e.* of ρ_{20}, the density of the substance in grams per millilitre at 20° C. Various standard specifications are appearing in respect of tar products, in which the limits for ρ_{20} are given as alternatives to sp. gr. limits. As the latter are based on $S_{15 \cdot 5° C./15 \cdot 5° C.}$, with the consequent introduction of alternative bases (*e.g.* $S_{38° C./20° C.}$, $S_{38° C./38° C.}$, $S_{38° C./15 \cdot 5° C.}$, $S_{38° C./4° C.}$, and $S_{20° C./20° C.}$) for such materials as creosote oil which deposit solids at 15·5° C., the choice of ρ_{20} should ultimately lead to a considerable simplification.

Standard Methods prescribes the use of either standard density bottles [4] or standard density hydrometers [5] for the determination of the value of ρ_{20} for tar and tar products; the high degree of accuracy attainable by the use of density hydrometers to the British standard specification, with the full application of modern hydrometer technique, is recognized, but until generally accepted, the density bottle must remain the instrument for referee tests.

When the determination is made at 20° C., the density of a liquid is given by $(W_{20}/V_{20})+A$, where V_{20} is the capacity of the bottle in ml.

[1] *Cf.* " Standard Definitions of Terms relating to Specific Gravity," (E 12-27), *A.S.T.M. Standards*, 1936, **11**, 1436.

[2] *B.S.* 718, 1936: " Density Hydrometers " (price 3s. 6d.), Appendix E.

[3] *B.S.* 554, 1934: " Report on Standard Temperature of Volumetric Glassware."

[4] *B.S.* 733, 1937: " Density Bottles."

[5] *B.S.* 718, 1936: " Density Hydrometers " (price 3s. 6d.).

and W_{20} is the weight in g. of liquid required to fill the bottle at 20° C., A being a buoyancy correction which is significant if accuracy to the third (and fourth) decimal place is required.

If the observation is made at a temperature other than 20° C., the determination of ρ_{20} involves the use of a combined correction for buoyancy and change in volume of the bottle and, of course, a correction for the change in density of the liquid. The calculation of ρ_{20} from ρ_t is made by use of the relation—

$$\rho_{20} = \rho_t + \beta(t-20)$$

in conjunction with the table below.

Change in Density (β) of Tar and Tar Products with Change in Temperature.

Product.	β in g./ml. per Centigrade degree.	Temperature range of applicability.
Crude tar	0·00065	15° to 25° C.
Refined tar	0·00065	
Crude benzole	0·00090	
Light oil	0·00080	
Middle oil	0·00060	15° to 40° C.
Benzole	0·00100	15° to 25° C.
Toluole	0·00090	
Xylole	0·00086	
Solvent naphtha	0·00085	
Heavy naphtha	0·00080	
Benzene	0·00105	
Toluene	0·00092	
m-Xylene	0·00086	
Crude carbolic acid	0·00070	
Crude cresylic acid	0·00075	
Refined cresylic acid	0·00080	
Crude tar bases	0·00089	
Refined pyridine bases	0·00085	
Pure pyridine	0·00097	
Refined heavy bases	0·00085	
Creosote oil	0·00075	36° to 40° C.
Anthracene oil	0·00070	15° to 25° C.

Note.—The values in the second column are necessarily only mean figures, as the actual figure will vary in the case of many products from sample to sample. They may only be used over the range of temperature indicated in the third column, and then only with a clear recognition of their limitations. In case of dispute, the need to apply a correction must be avoided by carrying out the test at the specified temperature.

The capacity (V_{20} ml.) of the bottle at 20° C. is $W'_{20}(1-\sigma/\Delta)/(\rho_{20}-\sigma)$, where W'_{20} is the apparent weight in air in g. of the water content at 20° C., ρ_{20} is the density in g./ml. of water at 20° C., σ is the density in g./ml. of the air at the time, and Δ is the density in g./ml. of the weights used.

The density of tar is usually obtained, when a density bottle is employed, by a slight modification of the foregoing principles, as mentioned under section VI (*a*), p. 136.

The use of a density hydrometer involves the taking of the reading under prescribed conditions, which have been laid down in order that the attention given to the design of the hydrometers themselves (with a view to the production of first class instruments) may not be negatived by ignorance of the influence of manipulation features. Corrections are required to the hydrometer reading (see below), and it would be illogical to introduce errors in the taking of the reading if later the application of the corrections assumes an accuracy of reading which was not achieved when the determination was made.

Except perhaps in case of doubt or dispute, most corrections to the observed hydrometer reading could probably be ignored, but *Standard Methods* recognizes the following as possibly significant, according to the degree of accuracy which is sought :—

(*a*) Correction for the scale error at the point of reading the hydrometer ;

(*b*) correction for the change in volume of the hydrometer between the temperature of the liquid tested, at the time of the test, and the temperature of adjustment of the hydrometer (20° C.);

(*c*) correction for the difference between the surface tension of the liquid and the surface tension for which the hydrometer has been adjusted ; and

(*d*) correction for the change in density of the liquid between the temperature of observation and the standard temperature 20° C.

It should be noted that the British standard series of hydrometers includes provision for hydrometers adjusted for use in liquids of different surface tension ; extreme variation between the surface tension of the liquid under test and the surface tension of calibration of the hydrometer used requires corrections amounting to upwards of 3 units in the third place of decimals. While such extreme conditions will probably rarely obtain, surface tension is a factor which might influence the result to a significant extent.

The foregoing considerations, both as to density bottle and density hydrometer determinations have reference to determinations of densities of liquid tar products. The only solid tar product for which density determinations are commonly required is pitch ; features of the method used therefor are given under section XI (*e*), p. 415.

(c) Specific Gravity.—There are alternative means of defining sp. gr.[1]; principally with a view to co-ordination with density

[1] *Cf.* " Standard Definitions of Terms relating to Specific Gravity " (E 12-27), *A.S.T.M. Standards*, 1936, 11, 1436.

considerations, *Standard Methods* defines sp. gr. as the ratio of the density of the substance at the temperature t_1 to the density of water at the temperature t_2. It is essential in all circumstances to specify both t_1 and t_2 when referring to the sp. gr. of a substance; the symbol S_{t_1/t_2} is used to indicate the ratio above defined.

The temperature 15·5° C. has been adopted for both t_1 and t_2 for tar and tar products technology, *i.e.* sp. gr. represented by the symbol $S_{15.5° C./15.5° C.}$ are used, except that, for light and middle oils which deposit soluble solids at 15·5° C., and for creosote oil, the sp. gr. $S_{38° C./20° C.}$ is used.

Standard Methods provides data for the conversion of sp. gr. to densities and for the conversion of sp. gr. hydrometer readings to density hydrometer readings; this information will become more useful as the change from the sp. gr. to the density basis of characterizing tars and tar products develops. This authority then deals with determinations, using alternatively a bottle or hydrometer method of test, and detailing the corrections to be applied in each case. The treatment of the subject is closely parallel to that for density determinations and calculations. In the absence of British standard sp. gr. hydrometers standardized by the British Standards Institution, full specifications for sp. gr. hydrometers appear in *Standard Methods* (see p. 437).

Definitions of terms relating to sp. gr. have already been cited in other works[1] and methods for converting sp. gr. at a known temperature to sp. gr. at a standard temperature have been detailed by the American Bureau of Standards.[2] American practice is discussed at length by Abraham,[3] who gives numerous references to a variety of methods.

(*d*) **Distillation.**—Distillation tests designed for commercial purposes have in the past been, and so far as can be seen will continue to be, based on empirical principles. The Standardization of Tar Products Tests Committee has effected considerable simplification, at least in the number of different test assemblies. Reference will be made, under the several groups of products, to the apparatus used for the distillation of members of each group, but certain common factors are discussed below in terms of general principles.

Standard Methods crystallizes unco-ordinated views on test points as follows:—

The **drip-point** is the temperature at which the first drop of distillate falls from the end of the condenser. *Standard Methods* observes that

[1] "Standard Definitions of Terms relating to Specific Gravity" (E 12-27), *A.S.T.M. Standards*, 1936, **11**, 1436.

[2] Circular No. 19, p. 43, 30th March 1916.

[3] Abraham, *Asphalt and Allied Substances*, London, 1929, p. 648, *cf.* 4th Ed. 1938, p. 788.

the temperature reading when 5 per cent. of the sample has distilled will indicate the presence of low boiling constituents more closely than will the drip-point, the use of which cannot be recommended.

The distillate obtained at a **stop-point** is that which is obtained when the specified temperature has been attained, and the flame having been removed or extinguished, the apparatus has been allowed to drain for (*a*) two minutes if the distillate coming over at the specified temperature consists essentially of low boiling products or of bases, and (*b*) five minutes in all other cases.

The distillate obtained at a **running-point** is that which is in the receiver when the specified temperature has been attained without interrupting the distillation at that temperature.

A specified temperature is to be regarded as having been attained immediately the top of the mercury column passes the corresponding point on the thermometer scale; this point will be the specified temperature reading or the corrected reading according to the instructions in the particular test which is being applied.

(The following practice for the determination of running-points is recommended as giving accurate results while requiring the services of only one operator :—

Accurate readings of temperatures and of the corresponding volumes of distillates shall be taken at approximately regular intervals throughout the distillation and shall include readings at temperatures approximating to the specified running-points. A temperature-volume graph is constructed, from which are read the volumes of distillate at the required temperatures, the latter having been corrected for barometric pressure if the instructions so require.)

The **dry-point** is the temperature at which the liquid just disappears from the bottom of the flask. The flame must be removed or extinguished immediately the distillation is complete, otherwise too high a temperature will be read. The temperature reading corresponding to a distillate of 95 per cent. of the sample is affected by small quantities of high boiling constituents and serves to detect these better than the dry-point which, under the conditions of distillation tests, is affected by superheating of the vapours, and the use of which cannot be recommended in the circumstances.

The **pitching-point** is the temperature at which (*a*) the temperature ceases to rise and begins to fall, and/or (*b*) fumes are evolved from the surface of the residue in the flask.

The **residue** in a fractionation test shall include the material which drains from the column into the flask after the removal or extinction of the flame. The draining period shall be (*a*) two minutes if low boiling products or bases are coming over when the flame is removed or extinguished, and (*b*) five minutes in all other cases.

Secondly, *Standard Methods* prescribes the corrections which are to be made, except where otherwise specifically indicated, to thermometer readings taken or used in the course of distillation tests. The first correction is that indicated on the certificate of the thermometer as issued by the National Physical Laboratory. The second correction is in respect of the atmospheric pressure at the time of the determination. For convenience, *Standard Methods* gives details of the corrections to be made to the observed barometer reading, and of the application of the corrected barometer reading to the correction of the thermometer reading (corrected previously for scale errors).

The effect of the difference between the prevailing barometric pressure and normal atmospheric pressure (defined as the pressure of 760 mm. of mercury at 0° C. and under standard gravity, 980·665 cm./secs.^{2}) is shown by the relationship

$$C = 0{\cdot}0011(760-P_0)(273+t_1)$$

(which is applicable to products consisting mainly of phenolic bodies) and

$$C = 0{\cdot}0012(760-P_0)(273+t_1)$$

(which is applicable to products consisting mainly of hydrocarbons), where C is the correction in °C., to be applied to the temperature t_1° C. observed at a prevailing atmospheric pressure of P_0 (corrected to 0° C. and, if need be, standard gravity), corrections to t_1 in respect of scale errors having first been made. The values of the right-hand parts of the above equations are given in the following tables over the ranges of values of t_1° C. and P_0 which are likely to be met with in laboratory practice.

The thermometers standardized in *Standard Methods* and prescribed therein for use in distillation tests are graduated for 100 mm. immersion measured from the bottom of the bulb. In use, the immersion is measured from this point to the top of the cork in the neck of the flask. The standard distillation flasks, which in the features at the moment relevant are those of the British standard series,[1] are so designed that if the top of the cork is about 10 mm. above the top of the neck of the flask and the immersion mark on the thermometer is level with the top of the cork, the bottom of the capillary of the thermometer is level with the lower edge of the side tube joint, as is required in the standard distillation tests. This system reduces errors of emergent stem to a minimum which may be ignored.

In test reports it is customary to indicate that the prescribed corrections have been made to distillation temperature results, by recording the temperatures as T° C. (corrected) or T° C. (corr.). Hereafter, all distillation temperatures referred to in connection with

[1] *B.S.* 571, 1934.

tests in *Standard Methods* are corrected temperatures unless the contrary be stated.

Correction of Temperature Readings for Barometric Pressure
Values of $0{\cdot}00011(760-P_0)\ (273+t_1)$
(*Correction to be applied for phenolic bodies*)

Pressure in mm. of mercury.	Temperature in Centigrade degrees.																	
	0.	25.	50.	75.	100.	125.	150.	175.	200.	225.	250.	275.	300.	325.	350.	375.	400.	425.
720	1·2	1·3	1·4	1·5	1·6	1·8	1·9	2·0	2·1	2·2	2·3	2·4	2·5	2·6	2·7	2·9	3·0	3·1
725	1·0	1·1	1·2	1·3	1·4	1·5	1·6	1·7	1·8	1·9	2·0	2·1	2·2	2·3	2·4	2·5	2·6	2·7
730	0·9	1·0	1·1	1·1	1·2	1·3	1·4	1·5	1·6	1·6	1·7	1·8	1·9	2·0	2·1	2·1	2·2	2·3
735	0·8	0·8	0·9	1·0	1·0	1·1	1·2	1·2	1·3	1·4	1·4	1·5	1·6	1·6	1·7	1·8	1·9	1·9
740	0·6	0·7	0·7	0·8	0·8	0·9	0·9	1·0	1·0	1·1	1·2	1·2	1·3	1·3	1·4	1·4	1·5	1·5
745	0·5	0·5	0·5	0·6	0·6	0·7	0·7	0·7	0·8	0·8	0·9	0·9	0·9	1·0	1·0	1·1	1·1	1·2
750	0·3	0·3	0·4	0·4	0·4	0·4	0·5	0·5	0·5	0·5	0·6	0·6	0·6	0·7	0·7	0·7	0·7	0·8
755	0·2	0·2	0·2	0·2	0·2	0·2	0·2	0·2	0·3	0·3	0·3	0·3	0·3	0·3	0·3	0·4	0·4	0·4
760	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
765	0·2	0·2	0·2	0·2	0·2	0·2	0·2	0·2	0·3	0·3	0·3	0·3	0·3	0·3	0·3	0·4	0·4	0·4
770	0·3	0·3	0·4	0·4	0·4	0·4	0·5	0·5	0·5	0·5	0·6	0·6	0·6	0·7	0·7	0·7	0·7	0·8
775	0·5	0·5	0·5	0·6	0·6	0·7	0·7	0·7	0·8	0·8	0·9	0·9	0·9	1·0	1·0	1·1	1·1	1·2
780	0·6	0·7	0·7	0·8	0·8	0·9	0·9	1·0	1·0	1·1	1·2	1·2	1·3	1·3	1·4	1·4	1·5	1·5

Correction of Temperature Readings for Barometric Pressure
Values of $0{\cdot}00012(760-P_0)\ (273+t_1)$
(*Correction to be applied for hydrocarbons*)

Pressure in mm. of mercury.	Temperature in Centigrade degrees.																	
	0.	25.	50.	75.	100.	125.	150.	175.	200.	225.	250.	275.	300.	325.	350.	375.	400.	425.
720	1·3	1·4	1·6	1·7	1·8	1·9	2·0	2·2	2·3	2·4	2·5	2·6	2·8	2·9	3·0	3·1	3·2	3·4
725	1·1	1·3	1·4	1·5	1·6	1·7	1·8	1·9	2·0	2·1	2·2	2·3	2·4	2·5	2·6	2·7	2·8	2·9
730	1·0	1·1	1·2	1·3	1·3	1·4	1·5	1·6	1·7	1·8	1·9	2·0	2·1	2·2	2·2	2·3	2·4	2·5
735	0·8	0·9	1·0	1·0	1·1	1·2	1·3	1·3	1·4	1·5	1·6	1·6	1·7	1·8	1·9	1·9	2·0	2·1
740	0·7	0·7	0·8	0·8	0·9	1·0	1·0	1·1	1·1	1·2	1·3	1·3	1·4	1·4	1·5	1·6	1·6	1·7
745	0·5	0·5	0·6	0·6	0·7	0·7	0·8	0·8	0·9	0·9	0·9	1·0	1·0	1·1	1·1	1·2	1·2	1·3
750	0·3	0·4	0·4	0·4	0·4	0·5	0·5	0·5	0·6	0·6	0·6	0·7	0·7	0·7	0·7	0·8	0·8	0·8
755	0·2	0·2	0·2	0·2	0·2	0·2	0·3	0·3	0·3	0·3	0·3	0·3	0·3	0·4	0·4	0·4	0·4	0·4
760	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
765	0·2	0·2	0·2	0·2	0·2	0·2	0·3	0·3	0·3	0·3	0·3	0·3	0·3	0·4	0·4	0·4	0·4	0·4
770	0·3	0·4	0·4	0·4	0·4	0·5	0·5	0·5	0·6	0·6	0·6	0·7	0·7	0·7	0·7	0·8	0·8	0·8
775	0·5	0·5	0·6	0·6	0·7	0·7	0·8	0·8	0·9	0·9	0·9	1·0	1·0	1·1	1·1	1·2	1·2	1·3
780	0·7	0·7	0·8	0·8	0·9	1·0	1·0	1·1	1·1	1·2	1·3	1·3	1·4	1·4	1·5	1·6	1·6	1·7

VI. EXAMINATION OF CRUDE TAR

Standard Methods demands a minimum of 5 gals. of crude tar for a full examination; the bulk of this is used in the distillation test and if a smaller quantity of sample is available, the large scale distillation test (p. 157) must be replaced by the small scale distillation test (p. 149). The results from the small scale test are not necessarily and will indeed rarely be comparable with those from the large scale test and are inevitably subject to considerable limitation of interpretation. The large scale test is therefore recommended for adoption wherever possible.

The withdrawal of test portions of crude tar from a bulk sample requires particular care. It is virtually impossible to withdraw a representative portion from a bulk sample which contains aqueous liquid in quantity which allows a clear layer to separate. In such circumstances the aqueous layer should be decanted and its weight and sp. gr., $S_{15\cdot5^\circ C./15\cdot5^\circ C.}$ determined. By weighing before decanting and allowing for the weight of the container of the bulk sample, the relative amounts of separated water and residual separated tar may be known.

This separated tar, or, if there is no separable aqueous layer, the original bulk sample is then thoroughly mixed to secure complete uniformity throughout the bulk immediately before any test portion is withdrawn. In the case of the more viscous tars, it is permissible to warm the sample to facilitate mixing and pouring, but a temperature of 60° C. must not be exceeded, and no source of intense heat should be used for warming the sample.

(a) Specific Gravity and Density

(i) The sp. gr. or density of the tar as received may be determined by the orthodox methods using a bottle, and this may prove satisfactory in the case of thin tars. Generally, however, and in any case with thick tars, the method is slightly modified by filling the bottle only partially with tar, and after weighing completing the filling of the bottle with water. This obviates the difficulty which is encountered when the stopper has to be forced home in the neck of a bottle completely filled with tar. In the case of a density determination, the density uncorrected for the buoyancy effect of the air is $W_2 \times {}_w\rho_t/(W_1 - W_3)$, where W_1, W_2 and W_3 are respectively the weights in grams of the water content of the bottle, the tar placed in the bottle and the water used to fill up the bottle after the tar has been weighed into the bottle; ${}_w\rho_t$ is the density of water at t° C. The weighings are assumed to have been made at that temperature and, if it is not 20° C.,

the density of the tar at 20° C. is calculated as described formerly, using the temperature coefficient shown in the table on p. 130, for crude tar.

The calculation of the sp. gr. in similar circumstances follows parallel lines, but does not involve the use of the density of water at t° C. as a factor in the formula. *Standard Methods* prescribes various facilitating and safeguarding operations which are advantageous or essential respectively, when determinations are being carried out on viscous materials such as tar.

The modification represented by only partially filling the bottle is an obvious extension of the use of a bottle for the determination of densities or sp. gr. of solid materials submitted for test in particle size sufficiently small to pass the neck of the bottle. Lunge [1] suggested a weighing bottle instead of the traditional form of density bottle, the stopper of the weighing bottle being provided with a vertical groove down its perimeter. The method, while introducing certain disadvantages, is nevertheless favoured in certain laboratories; the filling of the bottle is of course much easier and, in many cases, a limited amount of loss of accuracy is compensated for by convenience and expedition in carrying out the determination.

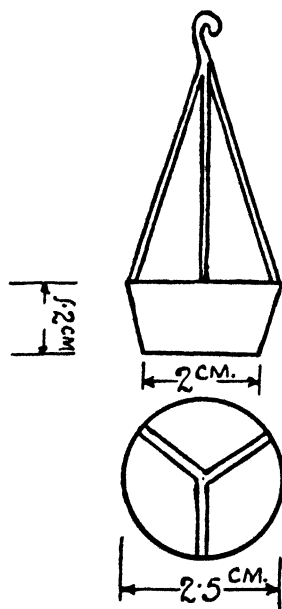
Fig. 28.

Weiss [2] employs a "platinum pan" method which is especially suitable for tars of a viscous nature. The use of the sp. gr. bottle, although recognized as standard, is described by Weiss as tedious, and considerable breakage of bottles occurs when numerous samples have to be handled. The pan (Fig. 28) is made entirely of platinum, the supporting wires being affixed with heavy platinum solder. The total weight is about 7 g. The weights in air and water at 15·5° are determined, the pan being suspended from the balance by a fine waxed silk thread. The pan is filled with tar and again the weights in air and water at 15·5° determined.

If A is the weight of the pan in air, B is the weight of the pan in water, C is the weight of the pan plus tar in air, and D is the weight of the pan plus tar in water, then the specific gravity of the tar is

$$\frac{C - A}{(C-A) - (D-B)}$$

The pan is rapidly cleaned by warming, pouring out the tar,

[1] *Z. angew. Chem.*, 1894, 7, 449. [2] *Ind. Eng. Chem.*, 1915, 7, 21.

immersing in benzole or naphtha and burning off. The method is stated to be quick, clean and accurate. Weiss also describes methods applicable when only small quantities of tar and oil are available. The tar, brought to the required temperature, may be drawn into a 1 ml. pipette to the graduation mark and there retained by a small piece of rubber tubing attached to the upper stem. After wiping the surface, the pipette, plus tar, is weighed. The appropriate weights of the pipette alone, and when filled with water at the required temperature, are then determined, and the sp. gr. of the tar calculated as formerly. The American Society for Testing Materials [1] specify the use of a pyknometer or weighing bottle, with the Lunge Modification (p. 137); detailed instructions are given for its use.

(ii) The sp. gr. of the anhydrous tar is obtained by calculation from the relationship $S = (100S_1 - S_2P)/(100 - P)$, where S_1 and S_2 are the sp. gr. respectively of the sample as received (after separating any decantable liquor) and of the decanted liquor, and P is the percentage by volume of water remaining in the sample from which any decantable liquor has been removed. This percentage is determined as described later.

If the sp. gr. of any separated liquor cannot be determined, or if there is no separated liquor, S_2 is taken as 1·01. Values for $S_{15\cdot5^\circ C./15\cdot5^\circ C.}$ are assumed throughout.

The density of the anhydrous tar may be determined in an exactly parallel manner.

(*b*) Water

As indicated previously, a bulk sample of tar containing separable water will have had any supernatant layer of aqueous liquor removed by decantation before the bulk sample is mixed prior to the withdrawal of a portion for test. (This is assumed in all subsequent references to the application of *Standard Methods* to crude tar examination.)

It will not be possible to decant all supernatant liquor from the bulk sample, while, of course, water will remain suspended in the residual tar or emulsified in it. *Standard Methods* prescribes the use of the Dean and Stark apparatus in conjunction with a glass or metal 500 ml. flask, for the determination of such residual water (see Fig. 86).

100 ml. of tar is measured at laboratory temperature into the flask, the receiver being washed with 100 ml. of solvent naphtha in successive portions, which are collected with the tar in the flask. Thick tars are weighed directly into the flask and 100 ml. of the naphtha added.

The apparatus is assembled and the flask heated so that two to five drops of condensate fall from the condenser per second. The

[1] "Standard Method of Test for Specific Gravity of Road Oils, Road Tars, Asphalt Cements and Soft Tar Pitches" (D 70-27), *A.S.T.M. Standards*, 1936, II, 1110.

distillation is continued until all the water has collected in the graduated tube. The rate of distillation is increased if a persistent ring of water forms in the condenser tube. Water droplets at the lower end of that tube are washed down with solvent naphtha introduced by a spray tube (see Fig. 85) which is passed down the central tube of the condenser. The water is measured in the graduated tube at the temperature at which the sample was measured. If more than 10 per cent. of water is present in the sample, it is necessary to withdraw water from the graduated tube during the course of the test, completing the withdrawal at the end of the test and using a standard measure to collect it.

A similar method has been standardized by the American Society for Testing Materials [1] for the determination of water in petroleum products and other bituminous materials ; this modification is being introduced for the determination of water in tar bitumen mixtures, in connection with certain British Standard specifications (now in course of preparation). A metal still or glass flask may be used, the former generally for tar and road materials and the latter for petroleum products. The still and flask are of the dimensions and shape shown in Fig. 29; the approximate capacity of the glass flask is 500 ml. The metal still is heated by a 100 mm. (3·94 in.) inside diameter ring gas burner, and the glass flask may be heated with an ordinary gas burner or electric heater. The collecting tube is graduated over 10 ml. in 0·1 ml. divisions correct to 0·05 ml., and a water-cooled condenser, having a jacket not less than 400 mm. (15·75 in.) in length and an inner tube 9·5 mm. to 12·7 mm. (0·37 in. to 0·50 in). in outside diameter, must be used. The solvent used for coal tars is a coal-tar naphtha or a light oil, 98 per cent. of which must distil between 120° and 250°. If the sample of material undergoing test contains more than 10 per cent. of water, the volume of material taken is reduced below the customary 100 ml., so that somewhat less than 10 ml. of water is collected in the graduated receiver. Connections between the flask or still and the condenser should be made by means of tightly fitting corks. A loosely fitting cotton plug should be inserted in the top of the condenser tube to prevent condensation of atmospheric water in the condenser tube.

The procedure with regard to rate of distillation is as stated in the Standard Method. Duplicate determinations should not differ by more than 0·10 ml. If the sample of tar has later to be used for other purposes, this method is not applicable. In these circumstances it is recommended that 25 g. should be weighed into an Erlenmeyer flask, through which a slow current of coal gas is passed. The flask is maintained at 105° for one hour, and the vapours, after passing through a reflux condenser, maintained at 50°, are passed into a tared

[1] (D 95-30), *A.S.T.M. Standards*, 1936, II, 997.

calcium chloride absorption tube. If the sample contains constituents volatilizing below 50°, the reflux condenser should be maintained at a correspondingly lower temperature. The moisture is determined by re-weighing the calcium chloride tube. Weiss[1] adopts direct distillation of 200 ml. of coal tar, with 150 to 200 ml. of dehydrated coal-tar naphtha or light oil, up to a temperature of 205°. The distillate

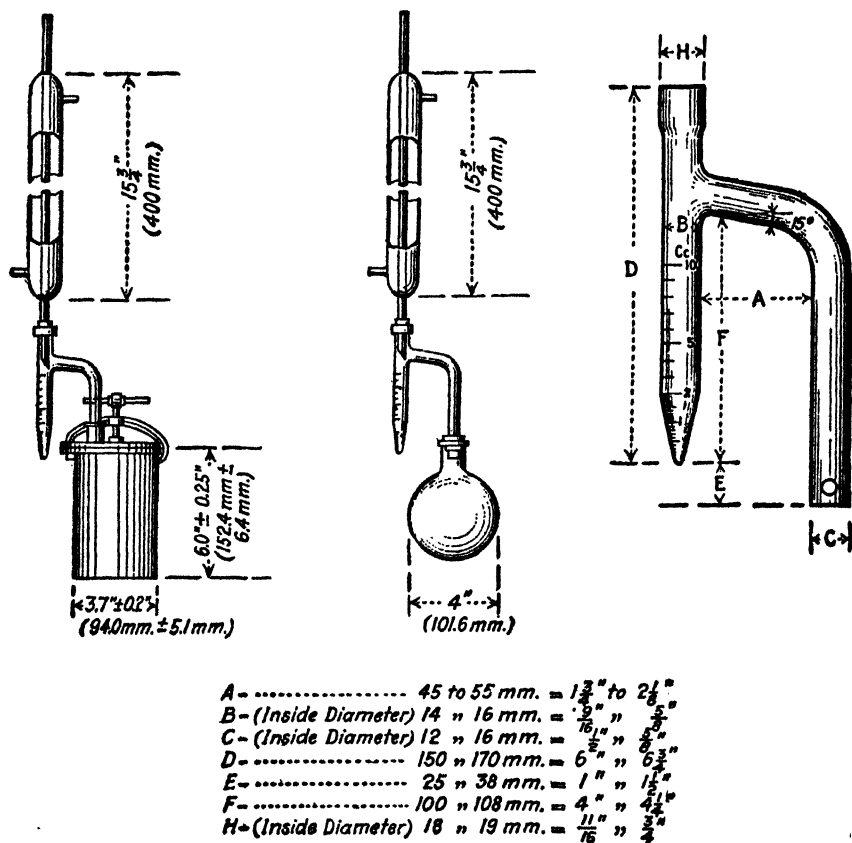



FIG. 29.

is collected through a condenser slightly inclined to the horizontal, in a graduated separating funnel, in which 15 to 20 ml. of benzole has been placed previously. The benzole effects a clean separation of water and oil. If dry tar is required, dehydration is carried out on 300 to 400 ml. of the tar, without the addition of naphtha, the 6 in. × 3½ in. internal dia. copper cylindrical still used in the direct distillation of the tar for the estimation of the water content being used for this purpose. Distillation is carried out cautiously until the vapour temperature reaches 170°, and the whole of the water has passed over.

[1] *Ind. Eng. Chem.*, 1918, **10**, 732.

The oily distillate, warmed sufficiently to dissolve any crystals which may be present, is separated from the water and returned to and thoroughly mixed with the residual tar in the still, after the residual tar has cooled to a moderate temperature. This method is substantially that recommended for tars, pitches, or creosote oils by the American Society for Testing Materials,[1] and accepted as the standard method by the American Association of State Highway Officials, the American Wood Preservers Association, the U.S. Bureau of Public Roads, and the American Gas Association. A temperature of 170° suffices to expel the whole of the water from the still, whereas a higher temperature is required in estimating the water content alone to ensure flushing out of the condenser tube. The simplicity and accuracy of the Standard Method render unnecessary the rather elaborate apparatus described by Becker,[2] in which the sample is distilled under vacuum, while that described by Senger[3] is similar to the apparatus used by Weiss (*loc. cit.*). Senger carries the distillation to a temperature of about 200°, and states that if the graduations in the receiver are obscured by the separation of crystals, the water should be filtered into a second cylinder through a small moistened filter paper. Other modifications of the method are designed to prevent excessive frothing of the tar during distillation.[4] Excessive frothing does not take place if the Standard Method is employed.

(*c*) Free-Carbon

The free-carbon in a tar is considered to be the material insoluble in a specified solvent (usually an organic compound or distillation fraction). *Standard Methods* recognizes the increasing knowledge of the constitution of the so-called " free-carbon " by preferring the title " insoluble matter " in connection with the essentially commercial test; the arbitrary choice of hot pure toluole to the British Standard Specification as the solvent to be used has been made principally on practical grounds, toluole being preferred to the more highly inflammable alternatives of benzole and carbon disulphide, or the less frequently available aniline and pyridine. The last four mentioned solvents have, however, their adherents, notably on the Continent.

Carbon disulphide is used particularly for bituminous material of an asphaltic nature,[5] a standard method being described by the

[1] (D 20-30), *Amer. Soc. Testing Materials, Standards*, 1936, **11**, 1053; (D. 246-33), *ibid.*, 542. [2] *J. Gasbeleucht*, 1902, **45**, 764. [3] *Ibid.*, 1902, **45**, 841.

[4] *Chem. Ind.*, 1887, **10**, 337; *Chem.-Ztg.*, 1902-3, **2**, 533; *Chem.-Ztg.*, 1909, **33**, 591.

[5] Avery and Corr, *J. Amer. Chem. Soc.*, 1906, **28**, 648; Richardson, *Proc. Amer. Soc. Testing Materials*, 1906, **6**, 509; Prévost Hubbard and Reeve, *Proc. Amer. Soc. Testing Materials*, 1910, **10**, 420; Prévost Hubbard, *Proc. Inst. Assoc. Testing Materials*, 1912, **xxv. 2.**

American Society for Testing Materials.[1] Adam and Sach [2] conclude that the character of the solvent employed is a much more important factor in the examination of pitch than of tar. Low-temperature tars are distinguished by the small amount of matter insoluble in such solvents as benzene, ether and chloroform, contents above 4 per cent. being exceptional in industrial low-temperature tars, an average range being from nil to 2·1 per cent. (pp. 94, 97). The amount present in low-temperature tars produced under carefully controlled temperature conditions in only one instance exceeded 1 per cent.[3] This material must not be confused with the resinoids of tar precipitated from solution in organic media by the addition of light petroleum. The latter bodies disappear as the temperature of carbonization increases and, owing to thermal decomposition of the low-temperature tar, tend to be replaced by the highly condensed and very complex bodies which constitute the free-carbon. Horizontal retort tars usually have a relatively high free-carbon content as compared with coke-oven and vertical retort tars, but the per cent. of free-carbon in horizontal retort tars may vary widely with the free space in the retort and with the temperature of the retort heating flues. Using retorts with a section of 22 in. × 16 in. there was an increase in the free-carbon content of the tar from 12·1 to 20·8 per cent. as the coal charge was progressively decreased from 35·5 lb. to 29·0 lb. per cu. ft. of retort space.[4] Free-carbon may contain varying quantities of inorganic matter present in the coal or coke dust mechanically entrained in the tar. Donath and Asriel [5] give the elementary analysis of free-carbon as C, 89·2 per cent.; H, 2·3 per cent.; N, 0·7 per cent., and O, 7·13 per cent., and Adam and Sach [6] state that the matter insoluble in benzene and carbon disulphide in Beckton pitch gave C, 90 per cent., and H, 2·79 per cent. Results of a like character are given by Hubbard and Reeve,[7] and by Weiss.[8]

Mallison [9] describes free-carbon as a complex mixture of hydrocarbons of high molecular weight, containing 90·0 to 91·7 per cent. carbon, 3·4 to 4·0 per cent. hydrogen, 1·0 to 1·2 per cent. nitrogen, 2·5 to 3·3 per cent. oxygen and 0·7 to 1·4 per cent. sulphur on the ash-free basis.

Hondurek [10] states that whereas benzene, toluene, pentane, ether, acetone, and glacial acetic acid cause a precipitation of certain resinous substances, other solvents such as aniline, quinoline, cresol,

[1] (D 4-27), *Amer. Soc. Testing Materials, Standards*, 1936, **11**, 1041.
[2] *J. Soc. Chem. Ind.*, 1929, **48**, 337 T.
[3] Morgan, *J. Soc. Chem. Ind.*, 1932, **51**, 67 T.
[4] Hollings, *J. Soc. Chem. Ind.*, 1926, **45**, 406 T.
[5] *Chem. Zentr.*, 1903, i. 1099.
[6] *J. Soc. Chem. Ind.*, 1929, **48**, 337 T.
[7] *Proc. Amer. Soc. Testing Materials*, 1911, **11**, 665.
[8] *Ind. Eng. Chem.*, 1914, **6**, 279.
[9] *Asphalt u. Teer*, 1935, **35**, 1001.
[10] *Mitt. Inst. Kohlenvergasung, Wien*, 1919, **1**, 9, 19, 28.

naphthalene oil and anthracene oil have no such effect. Adam and Sach [1] give the following results of using five different solvents.

	Insoluble matter in		Ratio:
	Tar.	Pitch.	Total insoluble in pitch. / Total insoluble in tar.
	Per cent.	Per cent.	
Toluene	12·7	26·0	1·25
Tetralin	11·5	20·2	1·075
Cresylic acid	11·0	18·6	1·03
Aniline	11·7	18·3	0·96
Pyridine	10·7	16·8	0·96

"The maximum difference of the insoluble matter content of crude tar as determined by different solvents does not exceed 2·5 per cent. on the weight of the tar but very marked differences are obtained with pitch. For high-temperature tars there is an approximately constant difference of the order of 1·5 to 2·5 per cent. between the percentages of matter insoluble in toluene and that insoluble in pyridine. The ratio of these two amounts varies with the type of tar." The matter insoluble in pyridine is identified in a general manner with matter truly suspended in the tar and termed by Hondurek [2] C_1 to distinguish it from C_2, the matter precipitated by benzene or toluene. Berl and Schildwachter [3] recommend the employment of tetralin under pressure for the direct determination of C_1. Microscopical examination shows that the suspended matter in the crude tar, C_1, is granular in nature, whereas that precipitated by benzene or toluene is of a bituminous resin-like nature, the fine grained free-carbon being collected within the resinous masses. Adam and Sach,[4] from an examination of various methods of distilling high- and low-temperature tars, conclude that "the formation of pyridine-insoluble matter in a tar during distillation indicates local overheating. In a modern distillation unit the formation ratio should approximate very closely to unity. For distillation to briquetting pitch, the final tar temperatures should not exceed 280° to 300°. The time of exposure of the tar to the maximum temperatures should be reduced to a minimum. The lower the temperature employed in the coal carbonizing process, the higher will be the alkali-soluble content of the tar and the greater its tendency to form toluene-insoluble compounds during distillation." Chemical interaction between the solvent and the precipitated matter is indicated by the separation of small amber-coloured crystals when gas tar is digested with chloroform [5] and by the presence of chlorine

[1] *Loc. cit.* [2] *Mitt. Inst. Kohlenvergasung, Wien*, 1919, **1**, 9, 19, 28.
[3] *Brennstoff-Chem.*, 1928, **9**, 137. [4] *Loc. cit.*
[5] Weiss, *Ind. Eng. Chem.*, 1914, **6**, 279.

in the free-carbon residues.[1] Selenium oxychloride is the best solvent for free-carbon, but the residues cannot be freed from the solvent. Free-carbon is decomposed by hot fuming nitric acid.

The Standard Method for the determination of insoluble matter (" free-carbon ") uses 2 g. of the sample of crude tar, warmed on a water-bath with 100 ml. of hot pure toluole (British Standard Specification quality). Settlement and decantation of the supernatant liquid follow, the latter being filtered through either balanced filter papers or a Gooch crucible. In general, laboratories prefer filter papers and the Standard Method prescribes in detail the manner of use of these. The residue is washed repeatedly with more of the hot toluole, then transferred to the filter and the washing continued. The residue on the filter is dried in an oven to constant weight. It is then incinerated, the weight of the ash deducted (allowing for the ash of the filter paper), and the percentage by weight of ash-free insoluble matter in the anhydrous tar is calculated.

The toluole must be maintained between 90° C. and 100° C. *Standard Methods* recognizes the applicability of the method in principle but with alternative solvents to replace the specified hot pure toluole; but such substitution must be indicated in the report on the test, which must record the matter insoluble in the specified solvent and *not* the " free-carbon " as defined in *Standard Methods*.

The Barrett Company of America use a method which is based upon that described by Weiss.[2] The tar should be dehydrated prior to extraction and freed from foreign substances by passage through a 30-mesh sieve. With materials containing less than 10 per cent. of free-carbon, 5 to 10 g. should be used, from 10 to 20 per cent., 2 to 4 g., and with more than 20 per cent., 1 to 2 g. If the content of material insoluble in benzole cannot be approximated, the larger amount should be taken. The form of extraction apparatus is shown in Fig. 30. The tar is weighed into a 100 ml. beaker and digested with 60 ml. of pure toluole at 90° to 100° for a period of not less than twenty and not more than thirty minutes. The whole is then decanted through a filter thimble which has been wetted with toluole previously. The thimble is made by shaping two filter papers (Whatman No. 50), one 12·5 cm. and the other 15 cm. diameter, placed concentrically round a cylindrical rod furnished with a 1 in. flat end and placed in the centre of the two filter papers. A cup about 2½ in. long, with the smaller paper inside, is thus formed. The beaker is washed with toluole until clean, all washings being passed through the thimble. The thimble is then washed with pure benzole and allowed to drain. The thimble is now covered with a

[1] Monroe and Broderson, *Ind. Eng. Chem.*, 1917, 9, 1100. *Cf.* Weiss, *ibid.*, 1918, 10, 400.
[2] *Ibid.*, 1918, 10, 732.

paper cone prepared by folding a 7 cm. filter paper in the customary manner, partially opening, pressing into position in a 60° glass funnel, and wetting with distilled water. In this position it is thoroughly dried. The empty thimble and cone are repeatedly washed with benzole to remove grease by extraction in the above apparatus for one half to one hour, and finally dried at 97° to 100°, cooling in a desiccator, and weighing in a weighing bottle after the expiration of

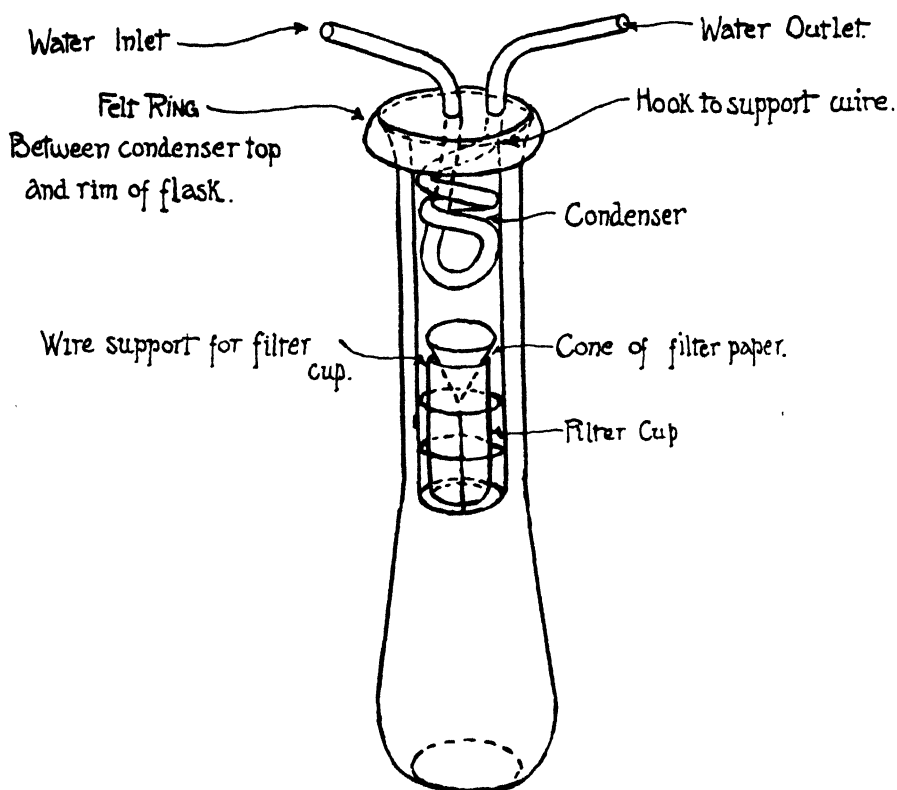



Fig. 30.

not less than fifteen and not more than thirty minutes. The used extraction thimble and cup are likewise placed in the extraction apparatus with a felt pad gasket around the top of the extractor to prevent loss of benzole, and extracted until the descending benzole is completely colourless, as shown by the evaporation of a few drops of the filtrate on a clean piece of filter paper. The thimble is then removed, dried at 97° to 100°, cooled in a desiccator for not less than fifteen nor more than thirty minutes and re-weighed. The increase in weight represents the free-carbon content. The accuracy is stated to be 5 per cent. of the insoluble matter present.

Variants on the above methods depend on the use of different solvents and differing quantities of tar.[1] Falciola, for example, uses olive oil. 5 g. of tar is added gradually to 125 to 150 ml. of olive oil heated previously to 140° to 160°. The mixture is then heated to about 180° to 190°, cooled to about 150° and filtered through a counterpoised filter paper. The residue of carbon is reheated with 50 to 75 ml. of olive oil at 180° to 190°. The oil extract is cooled to 150° and passed through the same filter paper. Finally the residue is transferred to the filter paper by means of carbon tetrachloride, and then washed with carbon tetrachloride or ether to free it from oil, dried and weighed. The amounts of free-carbon thus determined in various types of coal tar agree very closely with those obtained by Lunge's method. A complementary test is proposed by Nellensteyn and Kuipers.[2] 0·2 to 0·3 g. of tar is dissolved in nitrobenzene to give a 1 per cent. solution, by volume. The solution is allowed to cool and filtered through a specified filter paper. The microns are counted in a Thoma hæmocytometer at a magnification of 400, particles consisting of adhering smaller particles being counted as a single body. Different solvents will give different "micron" numbers. The test requires rigid standardization.

The "micron" number, which may vary between zero and 6×10^7 per cu. mm. of tar, is held to assist in evaluating the binding power, the better tar showing generally the higher numbers. A more exact value is given by the difference between the values obtained for the precipitates with a liquid of low-surface tension such as ether and one of high-surface tension such as nitrobenzene. The free-carbon determination is, however, adequate for all practical purposes.

(d) Fixed-Carbon

The fixed-carbon content of a tar is not usually required, test being more commonly applied to pitch in the course of the determi tion of its volatile matter and in differentiating various types of asp 'tic materials. The determination may be made in the same manne is for pitch (p. 427) except that greater precautions should be taken to guard against excessive foaming of the tar during the initial stages of heating. Abraham[3] adopts a modified procedure for the determination of the volatile matter of pitch according to the American Society for Testing Materials method for ascertaining the coke residue of creosote oil[4]:—1 g. of tar is weighed into a standard platinum crucible of 35 to 40 ml. capacity provided with a tightly-fitting capsule lid

[1] *Annali. Chim. Appl.*, 1917, **7**, 152.
[2] *Chem. Weekblad.*, 1928, **25**, 190; *Kolloid-Z.*, 1929, **47**, 155; *Gas World*, 1930, **92**, 54.
[3] *Asphalts and Allied Substances*, London, 1938, p. 949.
[4] (D 168-30). *Amer. Soc. Testing Materials*, *Standards*, 1936, **11**, 553.

which is pierced centrally with a 2 mm. hole. The crucible and contents are placed on a platinum, nichrome or fireclay triangle over a No. 4 Meker burner having an outside diameter of 25 mm. at the top, the flame of which is regulated to a height of 20 cm. when burning freely. The bottom of the crucible should be 6 to 8 cm. from the top of the burner. The tar is heated gently until the tendency to foam has passed, and then exposed to the full flame of the burner, so that a temperature of approximately $950^\circ \pm 20^\circ$ is reached. The desired temperature may be indicated by the fusion of crystals of potassium chromate in the crucible when heated in the specified position for the test. Full heating is continued for a period of exactly seven minutes. At the end of this period the crucible is transferred to a desiccator, allowed to cool, and weighed. Loss of weight represents volatile matter. The residue in the crucible, less the ash of the tar, is the fixed-carbon. The ash may be ascertained by igniting completely the residue but is best determined by a separate estimation (below). The test should be carried out in a position free from draughts. The under surface of the crucible lid should be free from carbon at the end of the ignition period. If this is not the case, any deposited carbon should be burnt off before weighing. Weiss [1] states the limits of accuracy of repeat determinations as 1 per cent. According to the American Society for Testing Materials Standards, a vertical electric tube furnace may be used, the temperature of which is regulated using a thermocouple.

In British practice the fixed-carbon content of a crude tar has not become a factor in sale and purchase, and consequently no method is prescribed in *Standard Methods*.

(*e*) Ash

The Standard Method starts with the distillation of a mixture of 100 g. of the sample and 50 ml. of dry heavy naphtha, using a standard distillation flask and air condenser, receiving the distillate in a 100 ml. graduated receiver; the distillation is stopped when 100 ml. of distillate has collected. The weight of pitch remaining in the flask is determined by difference weighing.

About 1 g. of the residual pitch is accurately weighed in a platinum or porcelain crucible, in which it is incinerated. The percentage ash content is calculated on the anhydrous tar.

Weiss recommends the use of 10 g. of tar and the use of platinum or porcelain crucibles. The heating should be carried out in a still atmosphere to prevent loss of ash.

[1] *Ind. Eng. Chem.*, 1918, **10**, 736.

(f) Viscosity

Standard Methods does not formally recognize the application of viscosity tests to crude tar; the Standard Method is classified therein as applied to refined tars, notably tars prepared for road purposes, roofing felts, etc. That method may conveniently be applied to crude tar provided the effect of water, particularly in small quantities, on the viscosity of tar is fully appreciated and taken into account.

Weiss describes the use of the Engler Viscometer[1] for the determination of the viscosity of crude tar. Dehydrated tar free from extraneous matter is heated on a steam-bath to about the correct temperature before being introduced into the viscometer, approximately 250 ml. being required. Dependent upon the consistency and nature of the material, temperatures of 77° F. (25° C.), 122° F. (50° C.), or 212° F. (100° C.) are employed. Up to 80° water may be used in the outer jacket; above this temperature a heavy lubricating oil is best employed.

When "specific viscosity" is required, the time of flow for a specified quantity of tar is divided by the time of flow of an equal volume of water at the same temperature.

According to Constam and Schläpfer,[2] the viscosities of various types of tar are as follows:—

	Viscosity (Engler).		
	20°.	50°.	100°.
Horizontal retort tar	42·7 to 150·0	4·35 to 25·6	1·46 to 2·39
Inclined retort tar	23·4 „ 114·7	3·65 „ 8·6	1·46 „ 2·18
Vertical retort tar	2·5 „ 51·9	1·51 „ 4·12	1·03 „ 1·44
Chamber oven tar	7·96 „ 13·46	2·02 „ 2·45	1·18 „ 1·22
Coke-oven tar	62·1 „ 149·1	4·93 „ 38·4	1·40 „ 1·73
Water-gas tar	1·81 „ 4·35	1·73 „ 1·88	1·02 „ 1·22
Oil-gas tar	1·52	1·15	1·01

(g) Ultimate Analysis

The ultimate analysis of a tar is determined by the methods commonly employed for the determination of the ultimate analysis of a coal (p. 2), that is to say, carbon and hydrogen by combustion of about 0·2 to 0·3 g.; sulphur by Eschka's method using 1 g. or by combustion in a calorimeter bomb, and nitrogen by Kjeldahl's method using 1 g. of tar; the oxygen is reported as a difference figure.

[1] Model A.H.T. 7688, or improved model A.H.T. 7690.

[2] *Z. Verein deutsch. Ingen.*, 1913, **57**, 1715.

Schläpfer gives the following ultimate analyses of coal tars [1] :—

	Carbon per cent.	Hydrogen per cent.	Oxygen and nitrogen per cent.	Sulphur * per cent.
Horizontal retort tar (Saar coal)	92·9	4·9	1·7	0·5
Inclined retort tar	90·2	5·9	3·4	0·5
Vertical retort tar (Ruhr coal)	88·0	6·8	4·7	0·5
Water-gas tar (Galician oil)	93·0	5·5	0·7	0·8
Oil-gas tar	92·2	6·3	1·1	0·4

* Cf. *Alkali Inspector's Report for* 1931, p. 25, London, 1932.

The chlorine content of crude tars has become of commercial interest and importance, presumably because of the recognition of ammonium chloride as a serious source of corrosion troubles in tar still practice [2] ; *Standard Methods* burns a sample of the tar (about 3 g.) with Eschka mixture. About 8 g. is mixed intimately with the tar in a platinum crucible and the mixture covered with 2 g. of Eschka mixture. The burning is done in the muffle furnace, gently at first and then, after about one hour, a dull red heat is maintained for two hours. The crucible and contents are allowed to cool and transferred completely to a beaker, using chlorine-free distilled water ; 35 ml. of pure nitric acid is added and the solution warmed ; excess 0·05 *N.* silver nitrate solution is added and the whole allowed to stand overnight.

After filtering and washing, the excess of silver nitrate is titrated with 0·05 *N.* potassium thiocyanate, using 2 ml. of iron alum solution as indicator. A blank test must be carried out. The Standard Method should be consulted for full operational details.

(*h*) Small Scale Tests for the Classification of Tar Samples

The laboratory examination of crude tars cannot be put on a routine basis which will result in records uniformly comparable with full scale plant operations in tar distillation. Nevertheless, bench tests are constantly required and, by the accumulation of parallel records of laboratory tests and plant practice on the same tars, useful guidance can be obtained, provided inferences from the results of the laboratory tests are not too far drawn. In practice, two sets of circumstances must be met : an admittedly rough distillation is required either because the amount of sample available is limited, or because facilities are not available or warranted for an unduly prolonged test ; secondly, a test is required which, while unlimited by the amount of sample available, will give the maximum amount of information and still be capable of performance on the laboratory bench.

[1] *J. Gas Lighting*, 1912, **118**, 297.

[2] Pratt, Ison and Wood, *An Investigation into the Causes and Prevention of the Corrosion of Tar Stills*, H.M.S.O., 1938, p. 7 *et seq.*

The former conditions are met by what *Standard Methods* describes as the small scale distillation test ; the latter conditions are met by the full scale distillation test described under (*i*) Commercial Assay, p. 153.

(1) Small Scale Distillation.—For the small scale distillation, a 450 ml. British Standard distillation flask is used in conjunction with a standard air condenser and standard thermometer, covering the range 90° to 400° C. A metal heating bath containing fusible alloy is used as the source of heat for the flask (see Fig. 31).

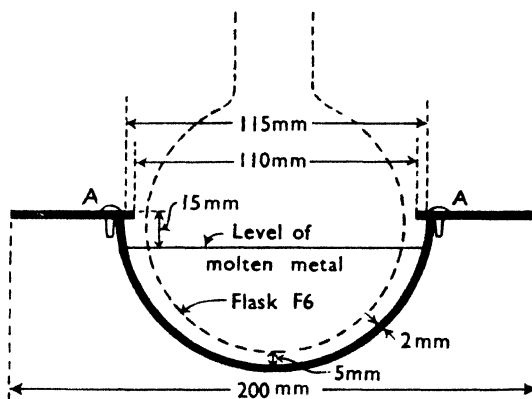
A known volume of the tar is dehydrated by distillation, in a standard flask of suitable size and through a standard Liebig condenser, until water ceases to come over ; after separation of the distillate, any oil therein is put back into the flask and the whole thoroughly mixed. About 250 ml. is then measured accurately into the 450 ml. flask and the apparatus assembled in the prescribed

Dimensions are minima.
A, A : Three or four pins or similar device to retain flange central, if flange and bowl not in one piece.

FIG. 31.—Small Scale Distillation of Crude Tar—Heating Bath.

manner. Details of the distillation procedure are given in *Standard Methods*, as also are particulars of a limited amount of examination of the fractions collected. The results available from the small scale distillation test are indicated by the table (p. 151), which shows the form in which it is suggested the report on the test should be made.

(2) Treatment with Solvents.—Research investigations, notably at the Chemical Research Laboratory, have led to a demand for examination of crude tars with a minimum decomposition of the original constituents. Solvent treatment methods have therefore come to be used in a limited sphere ; light petroleum causes a separation of the bodies termed resinoids [1] or rhetinols [2] ; a detailed account of the

[1] Morgan, *J. Soc. Chem. Ind.*, 1932, 51, 67 T.
[2] Edwards, *ibid.*, 1924, 43, 143 T, 149 T.

action of solvents on low-temperature tar (to which solvent treatment methods have been more particularly applied in practice) is given by Parrish.[1]

The method has not been widely adopted since it was first standardized in 1929. Consequently, the method was not revised

Analysis for Commercial Evaluation
(Small Scale)

Sample as received.	Specific gravity S 15·5° C./15·5° C.	Percentage by volume on sample as received.	Per ton or per 1000 gals. of sample as received.
Crude tar as received . .		...	...
Separated liquor . . .			gals.
Separated tar			,,
Unseparated liquor . . .	...		,,
Anhydrous tar . . .			,,
Chlorine (calculated as ammonium chloride) : per cent. by weight			

Fraction.	Specific gravity S15·5° C./15·5° C.	Condition after twenty-four hours at 15·5° C.	Caustic soda extract : per cent. by volume.	Percentage on sample as received		Content on anhydrous tar per ton or per 1000 gals.
				by volume	by weight.	
Up to 210° C.						gals.
210° ,, 230° C.						,,
230° ,, 270° C.						,,
270° ,, 300° C.						,,
300° ,, °C.						,,
Pitch		(Serial No. P.T.) test } :		° C.		cwts.
Loss on distillation : per cent. by weight						
Ash-free " free carbon " : per cent. by weight on anhydrous tar Ash : per cent. by weight on anhydrous tar						

for inclusion in the current edition of *Standard Methods*, and the 1929 version, summarized below, stands unaltered.

The test must be carried out on the dehydrated tar, but of course the removal of the water by distillation would be incompatible with the underlying principles ; the water is therefore removed by drying over anhydrous sodium sulphate, with frequent and intimate mixing.

[1] *Fuel*, 1926, 5, 436.

250 ml. of the dehydrated tar is mixed in a suitable flask with 500 ml. of 40°/60° light petroleum. The flask is fitted with a water-cooled reflux condenser and warmed on a water bath for two hours, the contents being shaken every ten minutes. With mobile tars a shorter period of heating will generally suffice. The cooled petroleum solution is now decanted and the pasty, insoluble residue re-extracted in like manner with two further quantities of 100 ml. of solvent. The combined petroleum extracts, after filtration, are exhaustively washed with successive quantities of a 10 per cent. aqueous sodium hydroxide solution, a large excess of soda being avoided. When extraction is complete the petroleum solution is exhaustively washed with water and then with a 25 per cent. aqueous solution of acetic acid to remove bases. The soda washings and acetic acid solution washings are reserved. The petroleum solution of neutral oils is freed from acid by washing with aqueous sodium hydroxide solution and water and then distilled from a weighed flask to remove the light petroleum. When the temperature of the vapour reaches 100° the distillation is interrupted, and then continued through a Young 12-bulb pear column until a temperature of 190° to 200° is reached. The fraction boiling below 200° is lost during this distillation, but the fraction is stated to be usually small. An approximation may be made from the amount of the fraction boiling below 200° as obtained during the straight distillation of the tar, after removal of the tar phenols. All the fractions boiling up to 350° are stated to be completely soluble in light petroleum. The weight of the residue boiling above 200°, and the sp. gr. at 15·5°/15·5°, are determined and the total percentage by weight and by volume of the neutral light-petroleum-soluble oils in the dehydrated tar thus calculated. The boiling range of the neutral oil may be determined by distillation under standard conditions at a rate of 5 ml. per minute, fractions being taken as follows :—200° to 240° ; 240° to 280° ; 280° to 320° ; 320° to 360° ; 360° to 400°, and residue at 400°. Any oil boiling below 200° is ignored. Standard conditions imply the use of a standard flask (No. F4, p. 447), a standard thermometer (No. T4 *a*, p. 436), and a standard air condenser (C1, p. 451). If distillation is carried out the sp. gr. of the fractions and residue should be ascertained as well as the temperature of complete homogeneity of any fractions containing solids at 15·5°.

The quantity of petroleum-soluble phenolic bodies is estimated by boiling the caustic soda extract to remove any neutral spirit, filtering and acidifying with mineral acid. The separated oil is transferred to a tared flask and the remaining aqueous layer twice extracted with benzole, the extracts being then added to the oil in the flask. The contents of the flask are then distilled through a Young 12-bulb pear column to remove water and benzole, the distillation being interrupted when the

temperature of the vapour reaches 170°. The residual oil representing the petroleum-soluble phenolic bodies is weighed and the percentage by volume and by weight on the dehydrated tar calculated. The sp. gr. is also determined.

The quantity of tar bases is usually too small for exact determination. An approximation may be arrived at by adding clear 40 per cent. aqueous sodium hydroxide solution to the acetic acid extract, the separated bases being run into a standard 50 ml. burette graduated to 0·1 ml. The separated oil is shaken with 40 to 45 ml. of 40 per cent. aqueous sodium hydroxide solution in the burette, allowed to separate, and the volume of residual oil ascertained. The sp. gr. of the bases may be assumed to be unity.

The whole of the petroleum-insoluble matter, including any material separated from the petroleum solution by filtration, is mixed with 250 ml. of pure benzole and warmed for one hour, using a reflux condenser. The mixture is then filtered through counterpoised filter papers on a perforated plate or through a sintered Jena glass filter plate using a slight vacuum. The insoluble matter is washed exhaustively with fresh benzole, dried at 100°, weighed, and its ash content then determined. The filtered benzole solution is distilled in a weighed flask through a Young 12-bulb pear column until a vapour temperature of 170° is reached. The residual petroleum-insoluble, benzole-soluble oil is weighed and the percentage by weight on the dehydrated tar calculated.

(*f*) Commercial Assay

The commercial assay of crude tar by distillation employing small quantities of tar cannot be relied upon to give concordant results. The quantities of distillates are, moreover, too small to allow of their detailed examination. The distillation test specified by the Barrett Company of America, although substantially that recommended by the American Society for Testing Materials,[1] the U.S. Bureau of Public Roads, and the American Association of State Highway Officials, is of this character. 100 g. (±0·1 g.) of the dehydrated sample is weighed into a flask of standard dimensions, which is then connected to a standard condenser, and supported as shown in Fig. 32. Heat is applied so that the first drop comes over in from five to fifteen minutes; thereafter distillation is conducted at a rate of between 50 and 70 drops per minute. Fractions are collected in tared Erlenmeyer flasks of 50 to 100 ml. capacity at points designated by specifications, or separate fractions are collected up to 170°; 170° to 235°; 235° to 270°; 270° to 300°. The residue above 300° is also

[1] (D 20-30), *Amer. Soc. Testing Materials, Standards*, 1936, II, 1053.

22 mm. ±1.0 mm. Inside Diam
Inside Diameter 10 mm ±0.5 mm
1.0 to 1.5 mm. wall
191 mm. ±1.5 mm.
99 mm ±1.5 mm.
Outside Diameter 86 mm ±1.5 mm.
220 mm ±5.0 mm
Distillation Flask
136 mm ±3 mm
27 mm ±1 mm
136 mm ±3 mm
105 mm ±2 mm
16 mm ±2 mm
32 mm ±0.3 mm
3.2 mm ±0.3 mm
76 mm ±3 mm
111 mm ±3 mm
Shield
Cover
Two Parts
6.4 mm ±0.5 mm
Flanged Open-End Cylinder Made of 22 gage Galvanized Iron with 1/8" Asbestos Lining Riveted to Metal
Shield
Thermometer
Cork Stopper
Shield
Retort
12 to 13 mm
2 Sheets Wire Gauze 20 Mesh
Chimney
Bunsen Burner
28.5 mm ±3 mm outside
Condenser
100 mm ±5 mm
360 mm. ±4 mm
50 to 60 cm
12.5 mm ±1.5 mm outside

Fig. 32.

reported. The results of the distillation are stated in percentages by weight of the dehydrated tar. The distillation apparatus is identical with that used in the Barrett distillation test of coal-tar oils, except that there are important differences in the position of the thermometer, the rate of distillation, and the cutting temperatures. In the present test the distance from the bulb of the thermometer to the outlet end of the condenser tube must not be more than 60 cm. and not less than 50 cm., no correction being applied for the emergent stem of the thermometer.

Even using larger quantities of tar, of the order of several litres, the results cannot be relied upon to reproduce manufacturing conditions exactly. Adam and Sach [1] have examined the results obtained by the Standard Method for the commercial analysis of crude tar, using a 5-litre iron still, directly heated by gas, to determine how far the results may be expected to agree with those obtained in large-scale practice. They conclude that " the flames impinging on the vertical walls of the still give rise to considerable cracking and that the pitch yields obtained will, therefore, be higher than should be obtained in large-scale practice." Their results are tabulated below :—

Process of distillation.	Nature of tar.	Pitch.		Per cent. insoluble matter.				Ratio: Total insoluble in pitch. / Total insoluble in tar.	
		Yield per cent. by weight.	Softening point °C. (Kraemer and Sarnow).	Tar.		Pitch.			
				C_1.	C_1+C_2.	C_1.	C_1+C_2.	C_1.	C_1+C_2.
5-litre iron still, gas heated . . .	Horizontal	59·2	81·3	10·6	12·4	21·5	32·4	1·20	1·55
5-litre iron still, gas heated . . .	Chamber oven	58·2	68·1	0·37	1·92	0·75	16·7	1·175	5·04
Wurtz flask, B.R.T.A. method * . . .	Horizontal	62·9	68·4	11·2	13·1	19·2	27·3	1·08	1·31
Wurtz flask, B.R.T.A. method * . . .	Vertical	50·0	58·3	3·15	3·8	6·9	13·2	1·09	1·74
Wurtz flask, B.R.T.A. method * . . .	Coke-oven	67·0	64·0	4·77	8·0	7·5	19·3	1·05	1·62
Wurtz flask ; oil bath ; maximum, 335° C. ; steam at 150° . .	Horizontal	55·6	85·6	11·2	13·1	20·3	28·1	1·007	1·19

C_1 = pyridine insoluble matter. $C_1 + C_2$ = benzene or toluene insoluble matter.

* British Road Tar Association Method.

The increase in C_1, representing insoluble matter formation, is very marked as compared with the Wurtz flask method used in standard road-tar analysis, the increased time of distillation in the 5-litre still being a contributory factor. A horizontal retort tar on distillation on

[1] *J. Soc. Chem. Ind.*, 1929, 48, 337 T.

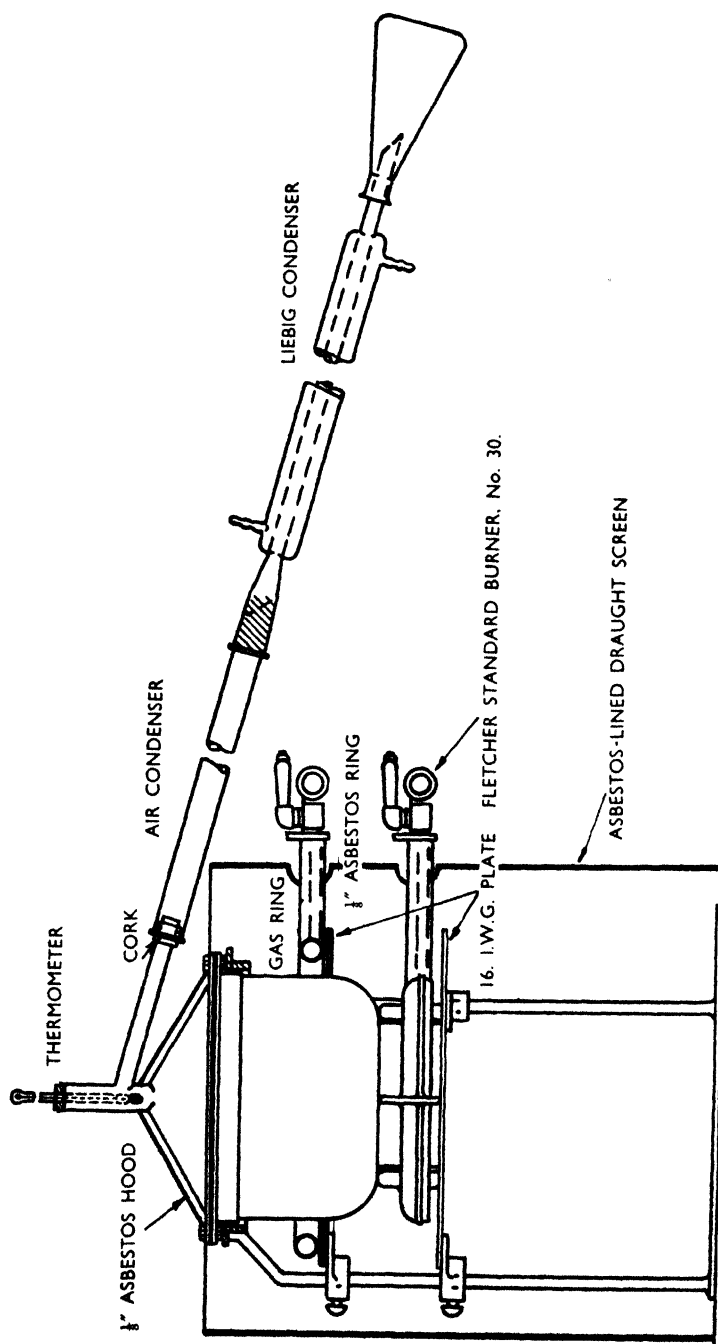



FIG. 33.—Full Scale Distillation of Crude Tar—Assembled Apparatus.

a large scale, in a Wurtz flask and in the 5-litre still, gave calculated insoluble matter ratios of C_1 0·96, 1·08 and 1·20, and of C_1+C_2, 1·26, 1·31 and 1·55 respectively. The nature of tar affects considerably the divergence which may occur between the results of large-scale practice and laboratory distillation assays. Low-temperature tars, and to a less marked degree, continuous vertical retort and intermittent chamber retort tars, undergo decomposition on heating, owing to the instability of their constituents at elevated temperatures. A bench size test is, however, in wide demand and can be employed to give data of considerable value, if properly used. *Standard Methods* employs the apparatus shown in Fig. 33, and gives full dimensional details of the apparatus there illustrated.

The complexity of and variation between crude tars makes it difficult to adhere to one detailed scheme of analysis, while the variations in full plant distillation practice make it impossible to lay down one obligatory scheme. The scheme outlined below is intended for selective adoption in any particular circumstances.

The three charts on pages 158 and 159 illustrate the scheme and correspond to three broad groups of the analyst's requirements, viz. :—

Chart I represents the **primary distillation.**

Chart II covers additionally the **extraction of crude phenols, naphthalene and anthracene,** together with a fractionation for evaluation purposes and for checking yields against large scale operations.

Chart III illustrates the **more complete analysis,** giving yields of benzole, toluole and naphthas, as well as pyridine bases and phenolic fractions in approximately commercial grades. This scheme of analysis should be useful in providing a standard procedure for the detailed analysis of crude tars.

If a detailed analysis is intended in respect of any of the separated products, as suggested particularly in Chart III, it will probably be necessary to repeat the distillation on successive portions of the same sample, and bulk the corresponding fractions from the several still charges.

The still is charged with a weight of tar corresponding to 5 litres at laboratory temperature, the still having been previously weighed. Distillation is carried out slowly while water is coming over, the principal source of heat being the burner surrounding the still, only a small flame being maintained on the bottom of the still at this stage.

When oil distils freely, the upper flame is put out and the heating by the lower flame increased so that the maximum rate of distillation compatible with complete condensation is achieved ; the minimum distillation rate at this stage is 9 ml. per minute. The Liebig condenser

CHART I: Primary Distillation of Crude Tar

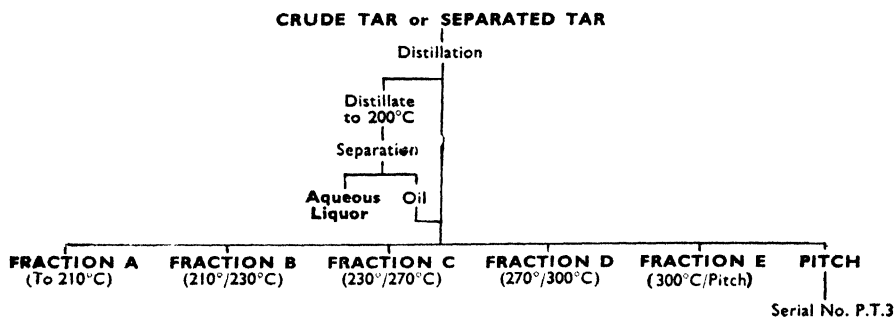



CHART II: Partial Analysis of Crude Tar

CRUDE TAR or SEPARATED TAR

Distillation

FRACTION A (To 210°C)

FRACTION B (210°/230°C)

FRACTION C (230°/270°C)

FRACTION D (270°/300°C)

FRACTION E (300°C/Pitch)

PITCH

Serial No. P.T.3

Separation

Aqueous Liquor

OIL

Washed with 10 % NaOH

Washed Oil

Sodium Phenates

Fractionation

Boiled and acidified

Wet Crude Phenols

FRACTION A′ (To 195°C)

FRACTION B′ (195°/230°C)

FRACTION C′ (230°/270°C)

FRACTION D′ (270°/300°C)

Residue E′

Cooled to 15·5°C

Cooled to 15·5°C

Cooled to 15·5°C

Washed filtered Fraction B′

Deposit pressed

Washed filtered Fraction C′

Deposit pressed

Washed filtered Residue E′

Deposit pressed

Naphthalene (Part)

Naphthalene (Part)

Crude Anthracene

Setting-point

Setting-point

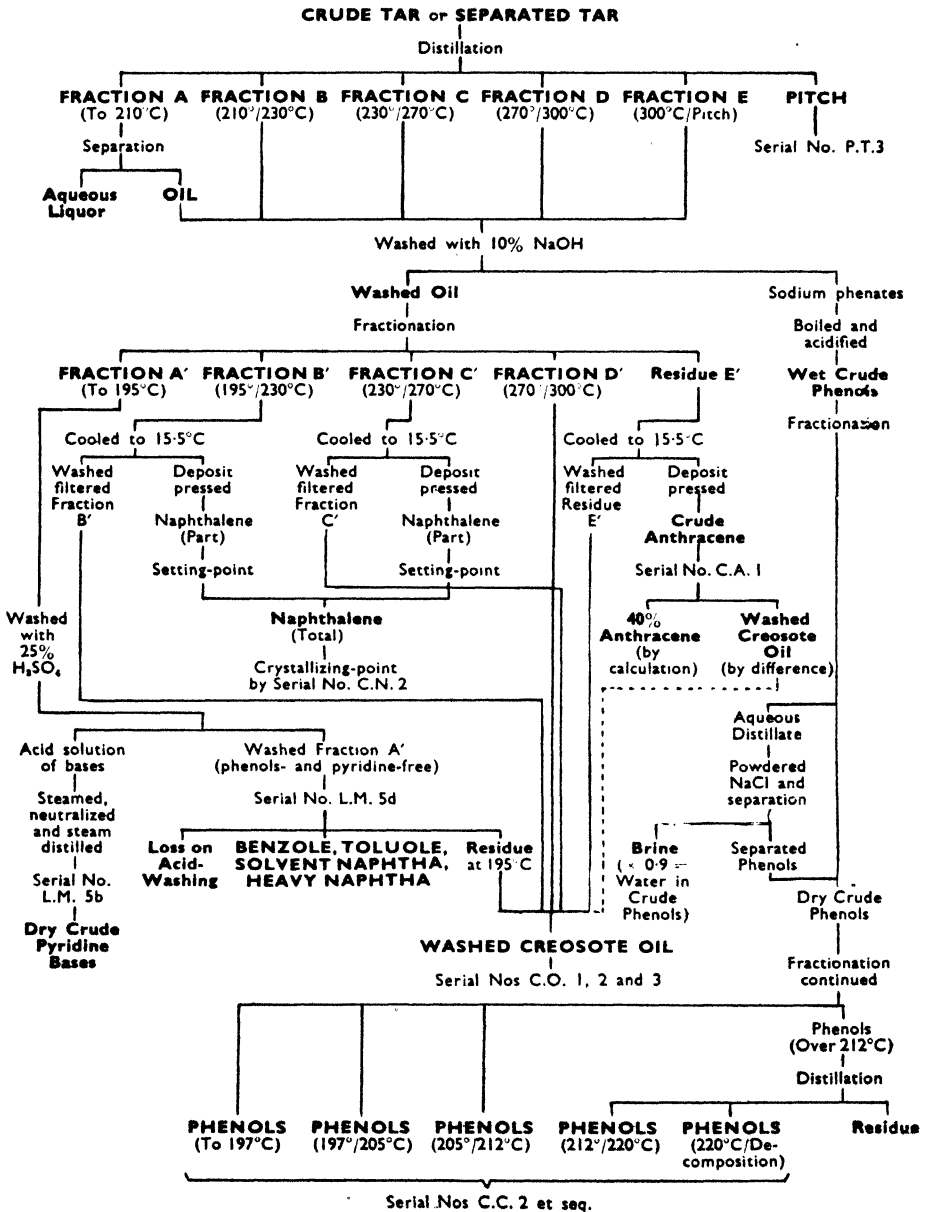
Naphthalene (Total)

Crystallizing-point by Serial No. C.N. 2

WASHED CREOSOTE OIL

Serial Nos. C.O. 1, 2 and 3

NOTE.—Products shewn in heavy type full capital letters (e.g. **CRUDE TAR**) are weighed and their specific gravities are determined. Products shewn in heavy type initial capital letters (e.g. **Aqueous Liquor**) are weighed but their specific gravities are not determined.

CHART III: FULL ANALYSIS OF CRUDE TAR

NOTE.—Products shewn in heavy type full capital letters (e.g. **CRUDE TAR**) are weighed and their specific gravities are determined. Products shewn in heavy type initial capital letters (e.g. **Aqueous Liquor**) are weighed or their quantities otherwise determined but their specific gravities are not determined.

is removed at 190° C. without stopping the distillation. If the scheme represented by Chart I is alone being applied, the oil in the distillate to 200° C. is added back to the still and the distillation resumed. Otherwise, the aqueous layer is taken from the fraction to 210° C. in order that the distillate to that temperature may not be affected by avoidable interruption of the distillation.

The broad principles of the distillation and subsequent treatment of the fractions are indicated in the charts and in the table; the latter is the form recommended for the analyst's report. The Serial Number references in the charts are to tests which are later described in the sections dealing with the products to which the numbers refer. *Standard Methods* must be consulted for the fully detailed instructions, on which reproducibility of results depends.

Explanation of the charts and table is desirable in respect of two points :—

(*a*) It will be noted that the *available* (washed) creosote oil, *i.e.* that obtainable for subsequent examination, consists of the following: (i) the residue at 300° C. from the fractionation after the removal of crude anthracene; (ii) the residue at 195° C. in the fractionation of fraction A′ (after that fraction has been washed for pyridine); (iii) fractions B′ and C′ after removal of naphthalene; and (iv) the distillate from 270° C. to 300° C. (fraction D′) in the principal fractionation.

The summation of the yields of these as an indication of the creosote content of the tar ignores oil losses in pressing the crude naphthalene and anthracene. An approximation to the *total* (washed) creosote oil may be obtained by taking the total weight of the residue over 300° C. and fractions B′, C′ and D′, and deducting the total weights of the naphthalene recovered and the 40 per cent. anthracene obtained by calculation in the determination of that constituent in Residue E′ from the principal fractionation.

(*b*) The results of the full scale distillation test are more valuable if the initial distillation is uniformly carried to a point at which a pitch of constant grade is obtained in the still. *Standard Methods* specifies pitch having a K. & S. figure of 70° C. In the absence of previous experience of the test or the particular tar under examination, the distillation may not be carried to the precise point at which such a pitch remains in the still. In such circumstances, the figure determined as the weight of the pitch yield in the still is adjusted so that the recorded figure is on a K. & S. 70° C. basis; to this end it is assumed that the addition of fraction E to the extent of 1 per cent. of the actual pitch yield lowers the K. & S. result by 2° C. The adjustment may only be made if the pitch actually obtained has a K. & S. figure between 60° and 75° C. and the test must be repeated if the figure falls outside that range.

Analysis for Commercial Evaluation of Crude Tar (including Full Scale Distillation Test)

	Specific gravity $S_{15 \cdot 5°}$ C./15·5° C.	Percentage on sample as received.	Per ton or per 1000 gals. of sample as received.
Sample as Received.		Per cent. by volume.	
Crude tar as received		...	...
Separated liquor			gals.
Separated tar			,,
Unseparated liquor	...		,,
Anhydrous tar		...	,,
Chlorine (calculated as ammonium chloride) . . . . . per cent. by weight.			
Analysis of the Tar.		Per cent. by weight.	
Total liquor	...		...
Crude fraction A : Up to 210° C. . .			gals.
Crude fraction B : 210° to 230° C. . .			,,
Crude fraction C : 230° to 270° C. . .			,,
Crude fraction D : 270° to 300° C. . .			,,
Crude fraction E : 300° to °C. . .			,,
Pitch, K. & S. 70° C. ( )* . .			cwts.
Loss by difference	...		...
Refractionation of Washed Crude Distillates.		Per cent. by weight.	
Fraction A′ : Up to 195° C.			gals. †
Fraction B′ : 195° to 230° C.			,, †
Fraction C′ : 230° to 270° C.			,, †
Fraction D′ : 270° to 300° C.			,, †
Residue : Above 300° C.	...		,, †
Partially Rectified Products.		Per cent. by weight.	
Loss on acid-washing	...		gals.
" Benzole " fraction : Up to 100° C. . .			,,
" Toluole " fraction : 100° to 120° C. .			,,
Solvent naphtha : 120° to 160° C. . .			,,
Heavy naphtha : 160° to 190° C. . .			,,
Phenols : Up to 197° C.			,,
Modified Lowe's test : °F. . .	...	...	...
Phenols : 197° to 205° C.			gals.
Phenols : 205° to 212° C.			,,
Phenols : 212° to 220° C.			,,
Phenols : 220° to °C.			,,
Dry crude pyridine bases	...		,,
Total washed creosote oil			,,
Crude naphthalene (crystallizing-point : °C.) . .			lb.
Crude anthracene (calculated as 40 per cent. anthracene) .			,,
Ash-free " free-carbon " : per cent. by weight on anhydrous tar.			
Ash : per cent. by weight on anhydrous tar.			

* Indicate here whether the figure for pitch of K. & S. 70° C. is "actual" (the pitch obtained in the test being of K. & S. 70° C.) or " calculated " (the pitch in the still being of K. & S. other than 70° C., the amount having been calculated to the basis of K. & S. 70° C. by means of the relationship given in the test).

† Fractions which cannot be conveniently measured by volume, by reason of their high temperature of complete fluidity, are to be returned in hundredweights in the third column.

As individual operators may prefer to work on the basis of other pitch tests as criteria in place of the K. & S. test, the following data are therefore given for the depressing effect of a 1 per cent. addition of fraction E to the pitch ·2° C. for the Ring and Ball test; 2·5° C. for the Half Inch Cube test. The corrections are applicable provided the pitch actually obtained tests not more than 10° C. below or 5° C. above the standard. All the pitch tests must be carried out by the Standard Method if the corrections are to apply; this is a matter of considerable importance in certain cases, as significant variations in the technique of pitch tests are widely known and recognized for purposes unrelated to the present considerations.

B. INTERMEDIATE PRODUCTS

The working up of coal tar consists of an initial distillation in wrought-iron stills which have a capacity up to 50 tons or in tube stills whereby the tar is fractionated according to works' conditions and market requirements for the final products. The names given to the various fractions vary, but in a general way the fractions are often designated according to their temperature of distillation as follows :—

1. The first distillate comprises crude naphtha obtained up to a temperature of 170°, together with a varying quantity of ammoniacal liquor. Accórding to *Standard Methods*, 1929, however, although the term " crude naphtha " obtains in certain parts of the country, owing to a gradual change in the nature of the products, the term has now become synonymous with " light oil."

2. Light oil may be considered generally to include the fraction boiling between 170° and 210°. According to *Standard Methods*, 1929, this fraction is defined precisely as a distillate from high-temperature coal tar containing commercial quantities of aromatic hydrocarbons distilling below 195°.

3. The creosote-oil fraction distils over between approximately 210° and 270°, and may be divided into light creosote oil distilling up to 230° and heavy creosote oil from 230° to 270°. According to the demand for anthracene, the heavy creosote oil and the final fraction (the anthracene oil) may often be run together and the whole fraction called heavy creosote oil. Anthracene oil is, however, marketed and it is necessary to distinguish this fraction. *Standard Methods*, 1938, defines creosote oil as oil distilling above approximately 200°.

4. Anthracene oil or heavy oil constitutes the fraction from 270° or 280° to the end of the distillation, which is determined largely by the desired quality of the residual pitch.

Prepared and dehydrated tars are now used in large quantities for many purposes, but particularly for the treatment of roads. In this event the crude naphtha, light oil and water alone may be removed or even some portion of the light creosote oil in addition ; the residual tar is then mixed with a heavy creosote. The separation of the fractions is controlled either by the temperature of distillation, or more generally by the sp. gr. of the distillate. A partial vacuum may be used to aid the distillation, and in some cases a continuous distillation process is employed. The fractions so obtained are subjected to further distillations, partly by the application of direct heat and partly by steam, in stills, either with or without dephlegmating columns, the phenols removed by treatment with alkali, the bases by treatment with dilute acid, the solid constituents (naphthalene and anthracene) separated by filtration and pressing, and the hydrocarbons finally purified, generally by treatment with concentrated sulphuric acid or by a special process (see p. 196). The yields of each fraction vary widely with the method of working adopted, as, for example, the degree of fractionation and the rate of distillation. A full description of the methods employed is given in standard text-books, such as those of Lunge and of Warnes.

The properties, composition, methods of examination, and the products obtained from each of the above fractions are described in the sequel, together with the most important methods of control.

It should be borne in mind that the Standardization of Tar Products Tests Committee bases the applicability of its tests on the following definitions for coal tar and the products for which tests are prescribed :—

Crude Tar.—A bituminous product, viscous or liquid, resulting from the destructive distillation of organic materials.

The word " tar " must always be preceded by the name of the matter from which it is produced : coal, shale, peat, vegetable matter, etc. Its mode of production should also be indicated. (Technical Dictionary of the Permanent International Association of Road Congresses.)

The following would be proper descriptions of the tars to which the present tests will normally be applied :—

" High Temperature Coal Tar (Horizontal Retort)."
" High Temperature Coal Tar (Vertical Retort)."
" High Temperature Coal Tar (Coke Oven)."
" Low Temperature Coal Tar."
" Oil Gas Tar " (" Carburetted Water-gas Tar ").

Refined Tar.—High temperature coal tar from which the water and more volatile oils have been removed by distillation.

Note.—The International definition reads : " A tar that has been distilled or cut back with the products of distillation, to the degree necessary to give a desired consistency." This corresponds more nearly to the definition for road tar below, while the Committee's definition for refined tar corresponds closely with the International definition for dehydrated tar.

Road Tar.—A product prepared by treating coal tar in such a manner that it conforms to a specification which defines its applicability for some branch of road work.

Benzole Forerunnings.—The first fraction distilled from crude or refined benzole or from light oil.

It contains a high proportion of constituents boiling below 75° C. and is usually rich in carbon disulphide; the forerunnings from unwashed benzole are usually rich in unsaturated hydrocarbons.

Crude Benzole.—A crude product extracted from coal gas, consisting essentially of benzene and its lower homologues, and having a sp. gr. $S_{15.5°C./15.5°C.}$ of at least 0·820 (or what is equivalent, a density $\rho_{20°C.}$ of at least 0·815 g./ml.).

Unsaturated hydrocarbons and sulphur compounds are usually present. Paraffins, naphthalene, phenols and pyridine bases may also be present, the last two usually in small amounts. Many crude benzoles will yield appreciable quantities of residue resulting from the oil used in their recovery.

Products having a similar distillation range are obtained by the distillation of crude tar.

Crude Low Temperature Spirit.—A crude product extracted from low temperature coal gases or tar and having a sp. gr. $S_{15.5°C./15.5°C.}$ lower than 0·820 (or what is equivalent, a density $\rho_{20°C.}$ lower than 0·815 g./ml.). The product will contain higher quantities of paraffins, naphthenes and unsaturated hydrocarbons than does crude benzole.

Solvent Naphtha.—A product conforming to a specification and consisting essentially of the xylenes and possibly higher homologues.

Heavy Naphtha.—A fraction of light oil or of crude benzole conforming to a specification and distilling substantially between 160° and 190° C.

Light Oil.—A crude fraction distilled from high temperature coal tar and containing commercial quantities of aromatic hydrocarbons which distil below about 190° C.

Phenols and bases are usually present.

Note.—The term "crude naphtha," formerly reserved for light oils containing a high proportion of low boiling hydrocarbons, is becoming obsolete.

Middle Oil or Carbolic Oil.—A fraction distilling substantially between 190° and 235° C., obtained from high temperature coal tar and containing commercial quantities of phenols and frequently of naphthalene.

Creosote Oil.—The oil or a blend of oils obtained from coal tar and distilling above about 200° C.

The term "creosote oil" should always be associated with an indication of the type of coal tar from which it has been produced, *e.g.* :—

"High Temperature Coal Tar Creosote Oil."
"Low Temperature Coal Tar Creosote Oil."

Creosote oil is usually made to a specification ; consequently the oil as obtained by the distillation of coal tar generally requires suitable treatment so that it will comply with such specification requirements.

Cresylic Creosote.—Creosote oil containing substantial amounts of phenols and usually conforming to a specification, especially in regard to its phenols content.

It may be obtained directly by the distillation of coal tar or it may be an oil in which the proportion of phenols has been adjusted to secure compliance with the specification.

Heavy Oil.—A high boiling creosote oil obtained from coal tar and distilling above about 270° C.

Anthracene Oil.—A heavy oil having a sp. gr. $S_{15 \cdot 5^\circ C./15 \cdot 5^\circ C.}$ above about 1·080 (or what is equivalent, a density $\rho_{20^\circ C.}$ above about 1·075 g./ml.), usually distilled from horizontal retort tar or coke-oven tar.

When the expression "anthracene oil" is used, there should always be an indication whether the oil is filtered or unfiltered.

Crude Anthracene.—The solid product, containing anthracene, obtained on cooling the coal tar distillate collected above about 270° C.

Coal Tar Phenols; Phenols.—The mixture of those constituents of coal tar or of coal tar fractions which are soluble in aqueous caustic soda solution.

The mixture consists essentially, but not always entirely, of monohydric phenols.

Phenol.—While the terms "coal tar phenols" and "phenols" have the meaning of the previous definition, the word "phenol" has been reserved throughout to indicate pure phenol, *i.e.* monohydroxybenzene.

Crude Carbolic Acid.—A crude mixture of monohydric phenols of substantial phenol content and complying with the applicability paragraph of the test described on p. 200.

Refined Carbolic Acid.—A mixture of monohydric phenols of substantial phenol content and refined to conform to a specification.

Crude Cresylic Acid.—A crude mixture of monohydric phenols, essentially cresols and higher homologues, of lower phenol content than crude carbolic acid.

Refined Cresylic Acid.—A refined mixture of monohydric phenols, consisting essentially of cresols and/or xylenols with or without a percentage of phenol.

Crude Naphthalene.—The solid product, consisting essentially of naphthalene, obtained on cooling crude intermediate fractions from the distillation of coal tar.

Crude naphthalene is also obtained during the purification of coal gas.

Refined Naphthalene.—Naphthalene commercially free from other hydrocarbons and from phenols, bases and other impurities.

Crude Tar Bases.—The mixture of those constituents of coal tar which can be extracted from the lower boiling distillates by dilute mineral acid. The mixture consists essentially of basic compounds of the pyridine series.

Refined Pyridine Bases.—A mixture of tar bases, consisting essentially of pyridine and its homologues, and refined to conform to a specification.

Refined Heavy Bases.—A mixture of the higher boiling tar bases, refined to conform to a specification.

Pitch.—The black or dark brown solid or semi-solid fusible and agglomerative residue remaining after partial evaporation or fractional distillation of tars and tar products (Technical Dictionary of the Permanent International Association of Road Congresses).

It is desirable that the derivation of the pitch be indicated, *e.g.* :—

"High Temperature Coal Tar Pitch."
"Low Temperature Coal Tar Pitch."

Note.—Pitches resulting from the distillation of tar oils and other tar products are not generally recognized in commerce. The Standard Methods for pitch as summarized on pp. 415 to 431 are intended to apply to normal commercial pitch which would properly be defined by the omission of the words "and tar products" from the International definition.

"Free-Carbon."—The solid carbonaceous matter remaining after the extraction of coal tar or pitch with pure toluole.

It is realized that so-called "free-carbon" is not composed entirely of carbon

and is actually a complex mixture, varying according to the solvent used. Pure toluole has been selected from among the solvents variously used, being the most suitable on practical grounds.

Tar Acids.—The use of the term "tar acids" has given rise to the belief that tar products contain acids comparable with the mineral acids in their corrosive action on, for example, metals. Where this belief prevails it is difficult to dispel it by argument. The Committee has consequently adopted the term "coal tar phenols" or "phenols" for use where the term "tar acids" would otherwise be used.

I. LIGHT SPIRITS, CRUDE NAPHTHA, LIGHT OIL, FORERUNNINGS, CRUDE BENZOLE

The oils recovered from coal tar by distillation, and boiling over a range of approximately 30° to 210°, are often described generally as *Light Spirits.* This term may also include similar oils obtained by the stripping of coal gas with wash oil or a solid adsorbent such as activated carbon. As explained previously, crude naphtha refers specifically to the first coal-tar fraction distilling up to 170°. Light oil may either denote a first coal-tar fraction distilling up to 195°, or, where the term crude naphtha is employed, light oil will define the second fraction boiling between 170° and 210°. The crude naphtha or light oil contains the crude benzole, the commercial products known as 50/90's benzole and 90's benzole being obtained by redistillation. Crude benzole is also recovered by stripping coal gas. The first fraction obtained on redistillation of the crude benzole, crude naphtha or light oil up to a temperature of about 70° to 80° is termed benzole forerunnings or fronts.

(a) Properties

1. **Light Spirits.**—The light spirits produced on carbonizing coal are divided between the gas and the tar in amounts which depend on the volume of the gas and the efficiency of the condensing system. Tars low in light spirits have, generally, been condensed at elevated temperatures and the light spirits are deficient in low-boiling constituents, notably benzole and toluole. In the United States most of the light spirits are obtained by gas stripping or from gas drips and amount to nearly 3 gallons per ton of coal carbonized, whereas that recovered by tar distillation rarely exceeds 0·5 of a gallon.[1] In Great Britain gas stripping is usual in the coke-oven industry for benzole recovery. Benzole is also recovered from coal gas in gas works.

The yields and compositions of the light spirits vary with the nature of the coal carbonized and the degree of cracking of the tar vapours

[1] Downs, *Chem. and Ind.*, 1932, 51, 28.

before leaving the retort or oven. Precise correlation of these with the rank of the coal is not possible. Under standard conditions of carbonization up to 625°, as the carbon to hydrogen ratio of the coal increases, the percentages of aromatic hydrocarbons in the total light spirits generally increase, and the percentages of unsaturated hydrocarbons decrease. The percentages of saturated hydrocarbons also increase slightly.[1]

Nature of coal.	Lota (Chile) coal. Meta-lignitous. Weakly caking.	Shafton. Para-bituminous. Weakly caking.	Dalton main. Para-bituminous. Medium caking.	Mitchell main. Para-bituminous. Strongly caking.	South Hetton. Ortho-bituminous. Very strongly caking.
Total yield of gas and tar spirit (gallons per ton of coal)	3·14	3·5	2·98	3·7	2·59
Analysis of blended spirit (refined) :—					
Aromatic hydrocarbons	29·9	23·7	33·4	39·5	36·9
Unsaturated hydrocarbons	35·8	39·4	28·0	17·5	21·7
Naphthenes and paraffins	34·3	36·9	38·6	43·0	41·4
Specific gravity at 15° C. :—					
Refined gas spirit	0·735	0·750	0·751	0·746	0·750
Refined tar spirit	0·795	0·810	0·805	0·812	0·820

The influence of the temperature of carbonization of the coal upon the yields and compositions of the light spirits is shown in the following tables[2] :—

Per cent. by Weight of Gas Spirit

Temperature of carbonization	450°	500°	550°	600°	700°
Yield in lb. per ton of coal	5·8	11·8	13·3	15·2	13·1
Total aromatic hydrocarbons	5·9	13·9	19·1	37·0	53·5
Unsaturated hydrocarbons	30·4	27·8	31·1	20·0	16·8
Saturated hydrocarbons and naphthenes (by difference)	63·7	58·3	49·8	43·0	29·7

Per cent. by Weight of Tar Spirit

Temperature of carbonization	450°	500°	550°	600°	700°
Yield in lb. per ton of coal	14·4	21·7	18·6	14·8	6·0
Total aromatic hydrocarbons	36·8	42·2	48·8	59·8	72·7
Unsaturated hydrocarbons	20·4	20·7	26·0	19·3	18·7
Saturated hydrocarbons and naphthenes (by difference)	42·8	37·1	25·2	20·9	8·6

[1] *Fuel Research Board*, Technical Papers, No. 17, 1927; No. 34, 1931.

[2] *Fuel Research Board*, Technical Paper No. 34, 1931; Ann. Report, 1920, 1921, Second Section.

Blended Proportionate to Yields given by the Gas and Tar Spirits

Temperature of carbonization.	450°.		500°.		550°.		600°.		700°.	
	Per cent. by weight.	Lb. per ton.	Per cent. by weight.	Lb. per ton.	Per cent. by weight.	Lb. per ton.	Per cent. by weight.	Lb. per ton.	Per cent. by weight.	Lb. per ton.
Aromatic hydrocarbons	27·9	5·6	32·3	10·8	36·4	11·6	48·2	14·5	59·5	11·4
Unsaturated hydrocarbons . . .	23·3	4·7	23·2	7·8	28·1	9·0	19·7	5·9	17·4	3·3
Saturated hydrocarbons and naphthenes . .	48·8	9·9	44·5	14·9	35·5	11·3	32·1	9·6	23·1	4·4
		20·2		33·5		31·9		30·0		19·1

The average composition of American coke-oven acid and base-free light spirits recovered by gas stripping and including gas drips from mains and holders is as follows [1] :—

	Per cent. by weight.
Benzene	55±
Toluene	15±
Xylenes, cumenes, trimethyl benzenes, etc. . .	10±
Coumarone, indene, and unsaturated compounds .	5±
Naphthalene and heavy oil	10±
Wash oil used for scrubbing coke-oven gas . .	5±

2. **Crude Naphtha** is a yellow to dark brown liquid of sp. gr. 0·840 to 0·940, with a penetrating odour reminiscent simultaneously of ammonium sulphide, carbolic acid and naphthalene. A green fluorescence of some specimens is due to tar mechanically carried over. Tars normally contain on the average 4 to 5 per cent. of crude naphtha but with high temperatures and light charges the amount is considerably less. The sp. gr. of crude naphthas of London make usually ranges from 0·883 to 0·888 and that of Scotch naphthas from 0·868 to 0·876 but the sp. gr. is sometimes considerably outside these limits.[2] Commercially, crude naphtha is understood to yield 20 per cent. or often 30 per cent. of distillate at 120° when distilled under the conditions of the retort test, whereas light oil should yield 50 per cent. at 200°. Allen gives the following figures, communicated by B. Nickels, showing the comparative behaviour of typical samples of crude and once-run naphthas when distilled in an ordinary retort and in a flask furnished with a bulb tube.

According to Lunge,[3] the crude naphtha (distilling over from the tar stills up to 170° or 180°) begins to boil at 80° to 90°, 30 to 40 per

[1] Downs, *Chem. and Ind.*, 1932, **51**, 28.
[2] Allen's *Commercial Organic Analysis*, London, 4th edn., 1914, **3**, 221.
[3] *Coal Tar and Ammonia*, London, 5th edn., 1916, **2**, 855.

cent. distils over up to 120° (the limit for benzole for aniline), 50 to 80 per cent. up to 160° (the limit for the xyloles) and the remainder, up to 90 per cent., between 170° and 220°. According to Spilker the light oil

Character of naphtha.	By retort method.			By bulb-tube method.		
	Below 100°.	From 100° to 120°.	From 120° to 170°.	Below 100°.	From 100° to 120°.	From 120° to 160°.
Crude—						
London . .	...	12	...	28	...	...
London . .	...	36	...	41	...	...
London . .	...	8	...	20	...	...
Plymouth . .	...	46	...	45	...	...
Lancashire .	...	20	...	25	...	...
Cleckheaton .	3	44	...	30	23	24
Derbyshire .	4	43	35	36	20	26
Scottish . .	...	28	...	32	17	37
Once-run—						
London . .	...	45	...	43	...	...
London . .	...	66	...	52	...	...
Country . .	...	60	...	45	...	...
Country . .	...	59	...	41	...	...
Country . .	...	58	...	42	...	...
Country . .	...	64	...	46	...	...

(defined as crude naphtha above), from coke-oven tar often contains much higher boiling fractions, and for such light oils the above percentages approach the upper limits ; were this found to be the case with gas tar, it would indicate a badly conducted distillation or an abnormally high percentage of water in the tar from which the light oils were obtained.

This difference is clearly shown in the following distillation yields from light oils from gas and coke-oven tars respectively [1] :—

Distillate.	Light oil from gas tar.	Light oil from coke-oven tar.
Up to 100°	10 per cent.	6 per cent.
Up to 135°	47 „	29 „
Up to 165°	69 „	42 „
Up to 195°	85 „	58 „
	Light oil from Vienna gas tar.	Light oil from Rhenish Westphalian coke-oven tar.
Up to 135° (crude benzole I.) . .	36·12 per cent.	12·66 per cent.
Up to 165° (crude benzole II.) . .	15·69 „	16·42 „
Up to 200° (carbolic oil) . . .	18·01 „	18·47 „
Residue heavy oil	26·51 „	46·36 „
Water and loss	3·67 „	3·09 „
	100·00 per cent.	100·00 per cent.

[1] Rispler, *Chem.-Ztg.*, 1910, **34**, 546.

J. von Hohenhausen gives the distillation ranges of crude naphthas as follows :—

Temperature °C.	Percentage of distillate.		
	Wigan.	Yorkshire.	Scotland.
105	...	4	...
110	4	16	17
120	19	34	38
130	33	47	49
140	45	...	58
150	55	...	69

According to Kraemer and Spilker crude naphtha contains the following classes of substances in the approximate proportions given :—

Phenols (tar acids)	5 to 15 per cent.
Bases (pyridines)	1 ,, 3 ,,
Sulphur compounds (carbon disulphide, thiophen and its homologues)	About 0·1 ,,
Nitriles	0·2 to 0·3 ,,
Neutral substances containing oxygen (acetone, coumarone)	1·0 ,, 1·5 ,,
Hydrocarbons	80 ,, 100 ,,

The last consist chiefly of aromatic hydrocarbons of which four-fifths is benzene and its homologues, and one-fifth naphthalene. The remaining hydrocarbons are olefines, 3 to 5 per cent. ; paraffins, 0·5 to 1·0 per cent. ; and cyclic hydrocarbons, both saturated and unsaturated, 1·0 to 1·5 per cent. The percentages of the individual benzene hydrocarbons in the mixture diminish as their boiling points rise (Kraemer and Spilker) ; the ratio of benzene, toluene, the xylenes, and tri- and tetra-methyl benzenes is approximately 100, 30, 15, 10 and 1.

Commercially, crude naphtha usually has a comparatively low percentage of tar acids, the average being about 4 per cent., but light oil is commonly sold with a guaranteed content of 20 per cent. of tar acids. Frequently the tar-acid content may be much higher, rising to as much as 28 to 30 per cent.

3. **Light Oil,** as it comes from the condensers, is a yellow or brownish oil possessing a slightly sharp but distinct odour of carbolic acid and naphthalene ; the sp. gr. (measured at 40° and calculated to 15°) is not below 1·00, and on the average amounts to about 1·02. Formerly, owing to the high naphthalene content, the

oil was solid or semi-solid at normal temperatures, but this is not usually the case now, although it may become so after the extraction of the tar acids, the naphthalene being soluble in the latter constituents. The oils which can be separated by draining or straining the mass should usually distil up to 250° and have a sp. gr. of 0·99 to 1·01. Kraemer and Spilker give the following results of the distillation of crude and of drained-off middle or light oil :—

Temperature ° C.	Crude oil.	Drained-off oil.
	Per cent.	Per cent.
160 to 170	5	4
180	10	10
190	20	25
200	35	43
210	55	58
220	70	75
230	80	81
240	85	86
250	88	88
255	90	90

The boiling points of light oils vary according to their origin.

Analyses of light oil produced by carbonization of 80 pound charges of coal in cylindrical retorts at varying temperatures are given by Kester and Holmes [1] as follows :—

Light Oil from the Carbonization of Mary Lee Coal

Temperature.	Olefines.	Naphthalene.	Refined light oil.	Paraffins.	Benzene.	Toluene.	Solvent naphtha.
° C.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
500	11·8	...	87·5	47·9	18·8	11·7	21·6
600	18·2	...	67·8	31·5	17·1	21·7	29·7
700	11·8	...	88·0	9·5	26·5	36·3	27·7
800	11·2	...	88·5	3·9	32·3	37·5	26·3
900	9·9	...	89·9	0·4	58·3	23·6	17·7
1000	5·4	...	93·7	0 9	76·2	11·4	8·5
1100	11·7	0·69	86·2	0·5	74·4	5·9	19·2

The above light oil represents tar spirit and spirit recovered from the gas by oil-stripping, and distillation of the wash oil up to 200°. The crude oil is refined with sulphuric acid (70 ml. of 1·84 sp. gr. acid per litre of oil) followed by steam distillation.

[1] *Ind. Eng. Chem.*, 1931, 3 (*Anal.*), 292.

Rispler[1] obtained the following results by working up the middle or light oils from gas tar and coke-oven tar :—

Distillates.	Middle oil from gas tar.	Middle oil from coke-oven tar.
	Per cent.	Per cent.
Up to 165°	4·15	1·78
Up „ 195°	21·77	19·91
Up „ 220°	43·45	28·68
Residue	26·91	48·18
Water and loss . . .	3·72	1·45

4. **Crude Benzole.**—In normal coke-oven and gasworks practice the nature of the coal is the most important factor in determining the yield of benzole. The quantities of benzole produced under similar conditions of carbonization from British coals are as follows [2] :—

Coal.	Gallons of crude benzole per ton.
Yorkshire	3·0 to 3·5
Lancashire	2·75 „ 3·25
Durham	2·5 „ 3·0
Midland and North Wales	2·0 „ 2·75
Cumberland	2·5 „ 2·75
Somerset	1·5 „ 2·0
Scottish *	1·5 „ 2·0
South Wales.	1·0 „ 1·5

* Some Scottish coals contain shale and give paraffinoid benzoles.

Hoffert and Claxton[3] confirm these figures for gases produced in coke-ovens and in horizontal gas retorts provided they represent the total amounts of " aromatic hydrocarbons " produced in the gas per ton of dry coal charged. The quantities of crude benzole actually recovered from the gas may differ considerably from the above, dependent upon the efficiency of recovery, the proportion of unsaturated constituents in the recovered product and the amount of wash oil left in the crude benzole. An average figure for all British coke-oven works is approximately two gallons of refined motor benzole per ton of coal carbonized. Concerning gasworks benzoles average analyses are given on the following page.[4]

[1] *Chem.-Ztg.*, 1910, **34**, 546.

[2] Whitehead, *Benzol*, London, 1920, p. 7.

[3] Hoffert and Claxton, *Motor Benzole, Its Productions and Use*, London, 1931, p. 325; cf. *ibid.*, 2nd ed., 1938, p. 42.

[4] Whitehead, *Benzol*, London, 1920; *cf.* Adam and Henderson, *Trans. Chem. Eng. Congr. W.P.C.*, London, 1936, **2**, 135; Delsol, *Int. Benzole Conf.*, 1934.

Per cent. by Volume

Retorts.	Specific gravity.	Paraffins.	Benzene.	Toluene.	Xylenes.	Unsaturateds loss on acid-washing.	Wash oil residue.
Horizontal . . .	0·896	1·3	50·3	16·4	8·0	5·6	17·7
Inclined	0·875	5·3	32·5	18·0	13·7	12·7	17·7
Vertical	0·860	12·6	26·7	11·5	20·1	11·0	17·7

Vertical retorts thus give a benzole containing larger quantities of paraffins and unsaturateds than that from horizontal retorts; benzole from inclined retorts is an intermediate product. As the temperature of carbonization decreases, so does the proportion of benzole to solvent naphtha. The composition of benzoles recovered by scrubbing the gas from steamed vertical retorts with activated carbon is given below [1] :—

Coal carbonized.	Steamed vertical retorts.			Horizontal retorts.
	Durham.	Yorkshire.	Yorkshire.	
Gallons of crude benzole per ton of coal carbonized	3·50	4·43	4·05	3·57
Loss on acid-washing, including "creosote" * formed . . .	19·46	25·43	26·82	13·92
Carbon disulphide	0·17	1·17	1·26	0·51
Paraffins	8·39	23·69	21·90	1·39
Benzene	50·74	32·42	35·01	64·87
Toluene	12·22	9·46	7·92	13·88
Xylene	3·91	3·90	2·47	0·84
Residue and loss	5·11	3·93	4·62	4·59
	100·00	100·00	100·00	100·00

* High-boiling residue left on redistillation after acid-washing.

Edwards [2] gives the following data relative to crude town's gas benzoles recovered by creosote washing :—

Per cent. by Volume

	1.	2.	3.	4.	5.
Benzene	52·23	56·90	54·01	55·42	50·70
Toluene	15·69	13·51	15·53	14·60	15·68
Solvent to 160° . . .	4·65	3·62	6·38	4·75	5·50
Creosote	17·02	16·48	15·07	16·82	17·87
Unsaturated hydrocarbons .	8·49	8·08	7·74	7·11	9·36
Carbon disulphide . . .	0·23	0·43	0·34	0·25	0·24
Paraffins to 139° . . .	0·68	0·88	0·89	0·94	0·62

[1] Hollings, Pexton and Chaplin, *Trans. Inst. Chem. Eng.*, 1929; *Cf.* Voss, *J. Soc. Chem. Ind.*, 1930, **49**, 343 T.
[2] *Gas J.*, 1917, **138**, 187.

Hoffert and Claxton[1] quote the following analyses of crude coke-oven benzoles of various strengths as shown by the amount distilling up to 120° :—

Sample.	1.	2.	3.	4.	5.	6.	7.	8.
Retort test.								
Per cent. by volume of distillate at 120° .	60·0	65·0	69·0	69·5	71·0	74·0	80·0	87·0
Composition per cent. by volume.								
Motor benzole . .	60·50	64·50	69·50	70·50	68·80	73·00	74·00	82·90
Solvent naphtha . .	7·00	6·00	5·00	1·80	7·50	5·50	8·20	4·00
Heavy naphtha . .	2·50	1·00	1·00	1·00	1·00	1·00	0·80	0·60
Creosote . . .	19·00	18·00	14·50	16·50	12·70	11·00	9·00	5·00
Loss on washing .	11·00	10·50	10·00	10·20	10·00	9·50	8·00	7·50
Refined motor benzole.								
Specific gravity . .	0·879	0·884	0·883	0·879	0·878	0·877	0·876	0·881
Distillation range (flask, per cent. by volume)								
Drip point, °C. . .	82·0	81·6	81·5	78·0	82·1	82·7	82·7	82·1
100° . . .	88·5	90·0	90·0	92·0	89·5	87·5	86·0	86·5
120° . . .	96·0	96·5	96·5	Dry at 117·0	96·5	96·5	96·5	96·5
Dry at °C. . .	120	123	124	...	124	125	123	122

Coke-oven benzole approximates in composition to benzole recoverable from normally charged horizontal gas retorts ; that is, the benzole contains a high proportion of aromatic hydrocarbons and is almost free from paraffins. In general the content of aromatic hydrocarbons increases with an increasing temperature of carbonization and prolonged exposure of the tar vapours to elevated temperatures but the yields decrease. Low temperatures and the reverse conditions of carbonization cause an increase in the unsaturated and paraffin hydrocarbons at the expense of the aromatic hydrocarbons. At abnormally high temperatures the yield of aromatic hydrocarbons may decrease owing to dissociation.[2] Hoffert and Claxton state that an excessive amount of paraffins in a benzole complicates and increases the cost of blending with petrol to produce a uniform quality motor fuel, whilst paraffins are objectionable in benzene and toluene for explosives manufacture and as solvents. The reduction of the quantity of paraffins present in crude coke-oven benzole by varying the conditions of carbonization, the amount of the coal charged and the size of the coal is discussed by Middleton.[3] Crude benzole recovered

[1] *Motor Benzole, Its Production and Use*, London, 1931, p. 324.

[2] Hollings and Cobb, *Trans. Inst. Gas. Eng.*, 1914, p. 254; *Gas J.*, 1914, **126**, 917; *cf.* McKee, *J. Soc. Chem. Ind.*, 1904, **23**, 403.

[3] *Gas J.*, 1920, **149**, 30; *Coke Oven Managers' Assoc. Year Book*, 1920, p. 63; *cf.* Tweedy, *Gas World*, 1931, **94**, Coking Section, 15.

by oil-stripping contains varying quantities of wash oil dependent upon the treatment of the benzolized oil in the debenzolizing still. If more or less complete recovery of crude benzole is effected, the crude benzole will contain a high proportion of wash oil ; the use of an incompletely stripped oil in the benzole scrubbers results in the production of a crude benzole containing a high proportion of benzene ; a large proportion of the toluene and higher homologues remain in the gas.

A crude benzole rich in toluene and the xylenes may be obtained if the wash oil is oversaturated.

*Effect of Over-Saturation and Under-Stripping of Wash-Oils.**

	Benzole (gal. per 10,000 cub. ft.).		Recovered.	Composition (per cent. by volume).	Per cent. efficiency of recovery.
	In gas, before scrubbers.	In gas, after scrubbers.			
Wash Oil A (over-saturation)					
Benzene . .	2·260	0·646	1·614	71·0	71·5
Toluene . .	0·479	0·076	0·403	17·75	84·5
Xylenes . .	0·254	0·0	0·254	11·25	100·0
Total benzole .	2·993	0·722	2·271	...	76·0
Wash Oil B (under-stripping)					
Benzene . .	2·21	0·270	1·940	80·5	88·0
Toluene . .	0·55	0·098	0·452	18·75	82·0
Xylenes . .	0·06	0·041	0·019	0·75	31·5
Total benzole .	2·82	0·409	2·411	...	85·5

* Hoffert and Clayton, *Motor Benzole, Its Production and Use*, London, 1938, p. 411.

Spielmann and Petrie [1] give the proportions of benzene, toluene and the xylenes present in nine samples of crude coke-oven benzoles as in table, page 176.

Besides aromatic and paraffin hydrocarbons, crude benzole may contain naphthenes [2] and small quantities of phenols and tar bases [3] ; traces of phenols, in particular, may influence the rate of resin formation.[4] In benzole recovered by means of activated carbon,

[1] *J. Soc. Chem. Ind.*, 1917, **36**, 831.

[2] Schneider and Konrad, *Gas- u. Wasserfach*, 1927, **70**, 1188.

[3] Smith, W., *J. Chem. Soc.*, 1874, **27**, 853.

[4] Hoffert and Claxton, *Motor Benzole, Its Production and Use*, London, 1931, pp. 334, 377 ; *cf. ibid.*, 2nd edn., 1938, p. 420.

hydrocyanic acid and other cyanides may occur and may, in like manner, actively assist resinification.[1]

Per cent. by Volume

	Benzene.		Toluene.		Xylenes.
	On crude benzole.	On distillate * up to 170° C.	On crude benzole.	On distillate up to 170° C.	On crude benzole.
1	48·3	57·0	21·0	24·8	4·0
2	55·5	69·0	13·0	16·1	2·0
3	49·6	69·2	10·3	14·1	2·5
4	52·0	63·5	14·9	18·2	4·0
5	65·5	69·1	13·9	14·7	2·5
6	39·0	50·9	15·8	21·1	4·0
7	45·6	53·7	19·0	22·4	6·0
8	57·7	66·1	13·1	14·9	3·0
9	36·0	38·7	22·0	23·5	7·0

* Representative of crude benzole free from wash oil.

The major impurities are carbon disulphide (up to 2·2 per cent.) and thiophen (up to 1·5 per cent.); traces of other organic sulphur-containing bodies as well as elementary sulphur are also often present. Olefines have been found in benzole forerunnings [2] and the diolefine cyclopentadiene has been isolated.[3] The latter may amount in some benzoles to as much as 1·2 per cent. by volume.[4] Indene is found in the fraction distilling between 176° and 187°,[5] and crotonylene [6] in the benzole forerunnings.

5. **Benzole Forerunnings.**—In *Standard Methods* benzole forerunnings (benzole fronts) are defined generally as the first fraction distilled from benzole, crude benzole or light oil, which contains a high proportion of low-boiling constituents including carbon disulphide, and in the case of unwashed products, unsaturated hydrocarbons. The temperature of distillation may be considered to be, broadly, 70° to 80°. For the production of motor benzole it is frequently collected with the once-run benzole, but in some instances it is collected separately with the object of reducing the sulphur content of the

[1] Hollings, Pexton and Chaplin, *Trans. Inst. Chem. Eng.*, 1929.

[2] Ahrens, *Z. angew. Chem.*, 1904, 17 (2), 1518; Lunge, *Coal Tar and Ammonia*, London, 5th edn., 1916, p. 211.

[3] Stobbe and Reuss, *Annalen*, 1912, **391**, 151; Auwers, *Ber.*, 1912, **45**, 3077; Stobbe and Dünnhaupt, *Ber.*, 1919, **52**, 1436.

[4] Gillies, *Gas World*, 1936, **105**, Coking Sect., 85.

[5] Kraemer and Spilker, *Ber.*, 1890, **23**, 3169, 3276.

[6] Koehler, Spilker and Weissgerber, *cf.* Lunge, *Coal Tar and Ammonia*, London, 5th edn., 1916, p. 219; also Caventou, *Bull. Soc. chim.*, 1863 (2), **19**, 245.

finished product.[1] According to Schultz [2] 50/90's benzole and 90's benzole contain 5 to 10 per cent. by volume and 10 to 27 per cent. by volume respectively of benzole forerunnings up to 81°.

(b) Examination of Light and Middle Oils, Benzole Forerunnings and Crude Benzole

1. **Examination of Light and Middle Oils** falls into two parts; first, a series of preliminary tests which, according to the end in view, may or may not be followed by a commercial analysis. The preliminary tests comprise the determination of sp. gr. and of the water content; a distillation test and the determination of the phenols in the distillate. The report of the results of these tests is supplemented by a statement on the general physical appearance of the sample, with special reference to the presence or absence of tarry matter, deposition of solids at normal temperatures and such other features as the analyst considers relevant.

The commercial analysis involves the isolation, with a view to subsequent examination, of phenols, pyridine bases, crude naphthalene and refined naphthas. The loss on acid-washing and the content of neutral oils are also ascertained.

Any sample of oil containing separated aqueous liquor must have such liquor removed, the quantity being noted, before any portion is withdrawn for test. Likewise, the sample must be thoroughly mixed before withdrawing portions and, if soluble solid constituents separate at normal temperatures, the container of the bulk sample must be immersed in a water bath to a temperature just sufficient to dissolve these soluble solids, the portions for test being taken from the warmed sample, the temperature of the sample at the time of withdrawal being noted.

(a) *Specific Gravity or Density.* These may be determined by any recognized Standard Method (p. 129), the sp. gr. $S_{38^\circ C./20^\circ C.}$ being determined instead of $S_{15\cdot5^\circ C./15\cdot5^\circ C.}$ in those samples which deposit soluble solids at 15·5° C. Factors for use when the determination is carried out at other than the standard on the basis of which the result is to be reported are given on p. 130.

The sp. gr. of a light oil varies with its boiling-point; normal light oils, of which about 90 per cent. boils below 200° C., have a sp. gr. of about 0·930. Values above 0·950 and below 0·900 associated with a 90 per cent. at 200° C. sample indicate an abnormal composition or admixture with other oils such, for

[1] Hoffert and Claxton, *Motor Benzole, Its Production and Use*, London, 1938, pp. 427, 480.

[2] Lunge, *Coal Tar and Ammonia*, London, 5th edn., 1916, p. 948.

example, as distillates of oil-gas tar or distillates from the lignite and petroleum industries.

(b) *Water. Standard Methods* prescribes a 500 ml. glass flask fitted with a standard Dean and Stark system. Two forms of receiver are available, the choice depending on the expected water content. The general procedure follows that summarized in connection with the determination of water in crude tar, except that solvent naphtha is added only if the sample does not distil smoothly and then only 20 ml.

(c) *Distillation.* The Standard Method prescribes a fully detailed distillation assembly. One hundred ml. of sample is distilled, the Liebig condenser initially employed being replaced by an air condenser at 200° C., which temperature constitutes a stop-point in the circumstances. Running-points and/or further stop-points are recorded as required until 95 ml. of distillate has been collected.

If water should accumulate during distillation, the test is carried out on a further portion of the sample after drying with finely powdered plaster of Paris, the report of the test stating that the preliminary drying was carried out.

(d) *Phenols.* The test for phenols in the preliminary examination of a light or middle oil is purely a determination, without any attempt being made to isolate the phenols for subsequent examination.

In the circumstances only a limited amount of material need be examined and the total distillate (from (c) above) serves the purpose. It is warmed, if necessary, until completely liquid and washed with 50 ml. of 10 per cent. caustic soda solution in a stoppered separating funnel. If necessary, in order to maintain naphthalene in solution, the caustic soda solution is also warmed. After settlement, the alkaline layer is removed and the residual oil washed with further successive but more limited quantities of caustic soda solution until all the phenols have been removed. Checking of complete removal is effected by slightly acidifying the last washings with concentrated hydrochloric acid and examining for separated phenols. A large excess of soda must be avoided, but there must be some excess.

The soda washings are collected in one receiver and boiled vigorously for ten minutes, maintaining approximately the initial volume by the addition of distilled water. The soda washings are cooled to laboratory temperature and transferred to the phenols flask (fig. 439) if clear. If not clear the solution is filtered through glass wool previously moistened with salt solution, the filtrate being collected in the phenols flask and the glass wool washed with the salt solution, that filtrate also being added to the phenols flask. Methyl orange is added and then concentrated hydrochloric acid until distinct acidity is evident after vigorous shaking ; the contents of the flask are kept cool during the acidification.

Just sufficient powdered salt is added to saturate the aqueous layer and leave a *few* particles undissolved. The phenols are brought into the graduated portion of the flask by the addition of saturated salt solution. After complete settlement their volume is read as that of the " wet crude phenols," as they always contain water which was not in the original oil.

Standard Methods contains fully detailed operational instructions and details of how the method is varied from the basic standard in the event of the phenols content being particularly low or high.

(e) *Commercial Analysis.* As previously indicated, the *Standard Methods* scheme for the commercial analysis of a light or middle oil makes available sufficient of those constituents present in substantial quantity for tests to be carried out on them. The analysis is carried out on 500 ml. of the sample for preference, though the amount may be reduced if the examination of the constituents is not to be carried very far.

If the sample will give good separation with caustic soda solution, the phenols are isolated as described below, using the sample itself. Otherwise the sample is distilled in the standardized assembly used for the preliminary distillation under (c) above, except that a larger flask is of course used. The measured 500 ml. of sample is distilled to 200° C. (stop-point) through the Liebig condenser, which is at that temperature replaced by the standard air condenser, the distillation being resumed and carried on until 95 per cent. of distillate has collected. The total distillate is used for the further examination.

(1) *Phenols.* Fundamentally, the treatment for the isolation of the phenols is that described in (d) above, except that, knowing the amount of phenols present, the amount of caustic soda solution required for washing may be calculated on the basis that 5 ml. of 10 per cent. soda solution will be required for the extraction of each ml. of phenols. The calculated amount of soda solution is used in two halves, so that two separate washes are given. Instead of the standard phenols flask, a separating funnel of suitable size is used to receive the carbolate solution, wherein the phenols are caused to separate with hydrochloric acid followed by powdered salt as before. Assuming that the phenols content is such that enough can be recovered for analysis, the resulting " wet crude phenols " are examined for their content of dry crude phenols and water. Alternatively, the crude phenols less water and residue on distillation may be determined, whereby the content of distilled crude phenols may be reported, or the examination may be completed by the determination of the phenol (C_6H_5OH) content. The methods for these examinations are referred to at greater length in the section dealing with Carbolic and Cresylic Acids, p. 197 *et seq.*

(2) *Pyridine Bases.* The phenols-free oil obtained under (a) above is fractionated in a standardized fractionating assembly which incorporates a 12-bulb column, and fractions are taken (i) up to 195° C. (stop-point), through the Liebig condenser and into a separating funnel ; (ii) from 195° to 250° C. (stop-point), through the air condenser and into a weighed conical flask. Fraction (i) is treated as described in the next paragraph ; fraction (ii) is reserved for the determination of naphthalene (see (3) below).

Fraction (i) is shaken for two minutes with one-fifth of its volume of 25 per cent. sulphuric acid and the mixture allowed to settle, when the acid layer is run into a round-bottomed flask and the washing repeated with a similar quantity of the acid. The combined acid washings are boiled for ten minutes and, on cooling, 20 per cent. caustic soda solution is added in sufficient quantity to neutralize the acid, the mixture being kept cool throughout. One hundred ml. of water is added and the mixture is distilled through a special assembly until the drops of distillate are substantially clear.

If the content of pyridine bases is limited, the examination from this point is necessarily limited to their determination. The aqueous distillate is made just acid to phenolphthalein by the cautious addition of 0·1 *N.* hydrochloric acid until the colour of added phenolphthalein indicator just disappears. Bromophenol blue indicator is then added and the mixture titrated with *N.* hydrochloric acid. If V ml. of *N.* acid is required, the weight in g. of commercial pyridine bases in the material examined is $0{\cdot}079 \times V$ in terms of pyridine ; the percentage by volume in the sample is obtained by using the assumed density of 0·982 g./ml.

If the pyridine bases are present in substantial amount they are isolated as follows : Solid caustic soda is added to the aqueous distillate until after thorough agitation the aqueous layer attains a sp. gr. of at least 1·35. On settlement, the upper layer, consisting of crude pyridine bases, is separated and agitated in a graduated measuring cylinder with sufficient solid caustic soda to leave a *few* undissolved particles. The mixture is allowed to stand for at least twelve hours and the volume of the pyridine layer noted. The material is available for such further examination as may be desired (see p. 349, under Pyridine Bases).

Standard Methods gives particulars of modifications which are permissible in the technique when the bases present in the original material contain significant amounts distilling above 195° C.

(3) *Naphthalene.* Commercial tests for naphthalene do not attempt to determine the total amount present in a tar fraction, but the amount which is deposited at a given temperature. Almost invariably this temperature is 15·5° C., but with certain fractions

required for special purposes lower temperatures are prescribed. The oils now under consideration are tested at 15·5° C.

Fraction (ii) from the fractionation of the phenols-free oil is weighed and, if necessary, warmed until completely liquid, when it is mixed thoroughly. Either 50 g. (or the whole fraction if less than 50 g. is available) is cooled to 15·5° C. and, after seeding with a small crystal of naphthalene if no crystals have appeared by then in the cooled fraction, the material is maintained within half a degree of 15·5° C. for four hours with occasional stirring.

The material is transferred to a cold Buchner funnel fitted with a rapid filter paper and as much oil as possible removed by the filter pump. The naphthalene is pressed between filter paper in a hand screw-press, the oily margins of the cake being removed and pressed separately. The utmost rapidity of operation must be maintained in the filtering and pressing processes. The naphthalene is weighed and its "corrected wet crystallizing-point" is determined (see under Crude Naphthalene, p. 297). The crystallizing-point must not be below 70° C. The approximate percentage of pure naphthalene may be ascertained as $2t - 60$, where t is the crystallizing-point as determined. If the sample freed from phenols distils completely below 195° C. in the fractionation, no fraction (ii) will be available for the naphthalene determination and naphthalene is assumed to be absent in such cases.

(4) *Loss on Acid-Washing.* The phenols- and bases-free material left in (2) above represents the starting-point for commercial marketable fractions of lower boiling products. It is first washed with acid to give an indication of the loss which will result from acid-washing on the works scale and to provide material suitable for the determination of the contents of commercial benzole, toluole and naphthas.

Acid-washing is carried out in a stoppered separating funnel, using 5 per cent. by volume of $95 \pm 0{\cdot}5$ per cent. sulphuric acid. If unsaturated hydrocarbons are present in substantial amount, extreme caution is necessary in the addition of and shaking with the acid, and vigorous cooling may have to be carried out. The pressure is released at intervals during shaking, by inverting the funnel and opening the tap. Shaking is continued for ten minutes and is vigorous as soon as the reaction is under control. On settlement, a small quantity of water is run gently down the side of the funnel, with as little disturbance as possible. The water gradually forms an intermediate layer and the acid and water layers may readily be run off; they are discarded and a little more water is introduced and worked round the inside of the funnel to remove acid tar there deposited. The operation must be carried out gently or an obstinate emulsion will be formed. This washing is also discarded after settlement.

Clear caustic soda solution is agitated gently with the remaining

naphtha, until its colour becomes yellow or brown and no further colour change is noticeable. The loss on acid-washing is the difference between the volume of the naphtha layer before and after treatment, plus the water subsequently recovered from the acid-washed material.

(5) *Commercial Fractions.* The contents of the commercial fractions—benzole, toluole, solvent naphtha and heavy naphtha—in the residual heavy naphtha are determined by fractionation in the standardized apparatus, fractions being taken as follows :—

Up to 100° C.	Commercial benzole.
100° ,, 120° C.	Commercial toluole.
120° ,, 160° C.	Solvent naphtha.
160° ,, 190° C.	Heavy naphtha.

each temperature being a running-point except the last which, of course, is a stop-point. Modifications in procedure are required to correct for the error which arises in the figure for commercial benzole, in the event of the distillation temperature rising rapidly when it has passed 100° C. The sp. gr. of the fractions give some indication of their respective paraffins contents.

(6) *Pure Products.* Instead of the commercial fractions mentioned under (5) above, it may be necessary to know the amounts of pure benzene, toluene and zylenes present. In that event the acid-washed material is subjected to examination by the Colman and Yeoman test (see p. 238).

For the simple distillation of the products in this section, the Barrett Company employ for the testing of light oil a distillation apparatus which is substantially that used by them for the distillation of benzole, toluole and xylole [1] (p. 224).

A standard American Society for Testing Materials High Distillation Thermometer [2] is, however, employed, and for materials having dry points substantially above 250° no asbestos board is interposed between the flask and the source of heat. If the oil boils substantially below 145° the flask is supported on an asbestos board provided centrally with a 1½-in. hole. After extraction of the tar acids from 100 ml. of oil, the residual oil is distilled at a uniform rate of one or two drops per second, the temperature of the first drop and of every 10 ml. of distillate being recorded. The volumes which have distilled at 130°, 170°, and 200° are also recorded. In the case of crude oils a decomposition point rather than a dry point is obtained. When decomposition is reached at the end of the distillation the temperature will cease rising and begin to fall. The highest temperature is noted as the decomposition point and the distillation is stopped. The fraction up to 130° approximates

[1] *Cf.* Weiss, *Ind. Eng. Chem.*, 1918, **10**, 1006.

[2] (D 20-30), *Amer. Soc. Testing Materials, Standards*, 1936, **2**, 1053.

to crude benzole and toluole; the 130° to 170° fraction represents crude solvent, and the 170° to 200° fraction represents the heavy naphtha.

These distillation ranges compare well with those obtaining in the method given by G. E. Davis,[1] which agrees in its essentials with that previously proposed by Lunge.[2] 200 ml. of the oil is washed for five minutes with 20 ml. of sulphuric acid of sp. gr. 1·84, followed by two washings with 300 ml. of water and then with 30 ml. of sodium hydroxide solution of sp. gr. 1·060. Finally the separated oil is washed with 30 ml. of water and measured. The oil is now distilled from a round-bottomed 200 ml. flask fitted with an efficient column and Liebig condenser, as many ml. of the washed oil being taken as correspond to the percentage obtained on washing. The flask is heated in a sand or air bath so that one drop passes over every two seconds. The distillate up to 120° is collected in a graduated cylinder, and the receiver changed to collect the portion passing over up to 170°. The burner is removed before each change of the receiver, and the condenser allowed to empty itself completely. The distillate up to 120° consists principally of a mixture of benzene and toluene; that from 120° to 170° is taken as solvent naphtha and gives by fractioning 90 per cent. boiling between 125° and 160°. The residue remaining in the flask, which generally solidifies on cooling, is considered as creosote oil.

For the approximate estimation of the products contained in the first fraction Davis gives the following tables (pp. 184 and 185).

Example. A sample of crude naphtha gave the following results by Davis's method :—

Loss on washing, 18·5 per cent.

Distillate up to 120° (benzene), 45 per cent.

Rectification of above, $\frac{100^\circ}{71} \cdot \frac{120^\circ}{94}$, *i.e.*, 50 per cent. of 90 per cent. benzole and 50 per cent. of 50 per cent. benzole, according to table A.

Distillate up to 170°, 10 per cent.

Rectification of same, $\frac{126^\circ}{0} \cdot \frac{160^\circ}{92}$.

The actual working results obtained in practice were :—

90 per cent. benzole, 23 per cent.
50 „ „ 24 „ } 47 per cent.
(*i.e.*, each about 50 per cent.).

Solvent naphtha, 10·4 per cent.

Rectification of same, $\frac{130^\circ}{1} \cdot \frac{160^\circ}{94}$.

Loss on washing, 20 per cent.

[1] *J. Soc. Chem. Ind.*, 1885, 4, 645.

[2] *Coal Tar and Ammonia*, London, 5th edn., 1916, p. 1000 *et seq.*

A. Mixtures of 90 per cent. and 50 per cent. Benzole

Benzole.		First drop. °C.	Percentage distilled at 100°.	Percentage distilled at 120°.
90 per cent.	50 per cent.			
0	100	92	50	90
5	95	92	51	92
10	90	91	51·5	92
15	85	91	53	92
20	80	90	55	92
25	75	90	60	93
30	70	90	65	93
35	65	90	67	94
40	60	88	69	94
45	55	88	70	94
50	50	87	71	94
55	45	87	73	94
60	40	86	76	95
65	35	86	78	95
70	30	86	79	96
75	25	85	84	96
80	20	85	84	97
85	15	84	86	97
90	10	84	88	Dry
95	5	84	89	,,
100	0	84	90	,,

B. Mixtures of 50 per cent. Benzole and Commercial Toluene

Mixture of		First drop. °C.	Percentage distilled at 100°.	Percentage distilled at 105°.	Percentage distilled at 110°.	Percentage distilled at 120°.
50 per cent. benzole.	Toluene.					
100	0	92	50	68	80	91
95	5	93	45	64	76	91
90	10	94	33	60	73	90
85	15	94	30	58	73	90
80	20	95	28	57	72	90
75	25	95	26	55	71	90
70	30	96	22	48	67	90
65	35	96	19	47	65	90
60	40	96	15	46	65	90
55	45	97	12	44	65	90
50	50	98	8	42	64	90
45	55	98	4	34	57	90
40	60	99	0	26	56	90
35	65	100	0	25	55	90
30	70	100	0	23	53	90
25	75	100	0	21	53	90
20	80	100	0	16	48	90
15	85	101	0	14	46	90
10	90	102	0	13	45	90
5	95	103	0	10	44	90
0	100	103	0	0	39	90

C. Mixtures of 90 per cent. Benzole and Commercial Toluene

Mixture of		First drop. °C.	Percentage distilled at 100°.	Percentage distilled at 105°.	Percentage distilled at 110°.	Percentage distilled at 120°.
90 per cent. benzole.	Toluene.					
0	100	103	0	7	50	94
5	95	102	0	21	59	94
10	90	101	0	30	66	94
15	85	100	0	38	68	95
20	80	97	9	43	73	95
25	75	95	16	53	76	95
30	70	95	23	59	78	96
35	65	94	33	60	80	96
40	60	93	43	66	82	96
45	55	92	46	71	85	97
50	50	91	52	72	86	97
55	45	91	58	76	86	97
60	40	91	60	78	88	97
65	35	90	65	81	89	97
70	30	89	71	83	91	97
75	25	88	75	85	91	98
80	20	87	77	87	92	98
85	15	86	83	89	93	98
90	10	85	85	91	94	Dry
95	5	84	88	93	95	„
100	0	84	90	94	96	„

For the separate estimation of benzene, toluene, xylene, carbon disulphide, and paraffins, including naphthenes in light oil, and light oil products, the Standard Method described on p. 238 should be employed. This method is only applicable to washed samples, unwashed samples being first treated with 95 per cent. sulphuric acid and the loss noted. According to this method the separate fractions are taken without interruption of the distillation. They comprise the fraction up to 90° (mainly benzene); 90° to 140° (mainly toluene with some benzene and xylene); 140° to 160° (solvent naphtha); 160° to 190° (heavy solvent naphtha), and residue above 190°. It will be seen that a general agreement of ranges of temperature is evident in the various methods described above.

2. **Examination of Benzole Forerunnings.**—When motor benzole is being produced the benzole forerunnings is often collected with the once-run benzole; in the preparation of refined products it is separately treated to reduce the sulphur content. The estimation of the carbon disulphide content of the benzole forerunnings may then be necessary, in which case, if this alone be required, the method described on p. 262 should be used. Occasionally it is necessary to know, in addition, the percentages of benzene, toluene, and paraffins including naphthenes. For this purpose the method described by

Spielmann and Butler Jones[1] has been adopted as the Standard Method. The method is summarized below :—

(a) *Toluene.* One hundred ml. of the sample, previously washed with 5 per cent. by volume of 95 per cent. sulphuric acid (p. 181), is distilled from a standard distillation flask (No. F 2, p. 447) at the rate of 2 ml. per minute, the usual precautions being taken and temperature corrections applied. The volume distilling below 90° is measured and referred to Graph 2 (A).

(b) *Carbon Disulphide.* The sp. gr. of the original sample is first determined. A sufficient quantity is then shaken frequently during one hour with half its volume of a 10 per cent. solution of sodium hydroxide or potassium hydroxide in nearly anhydrous alcohol. The alcohol used must be pure ethyl alcohol (which need not be absolute), or industrial methylated spirit free from paraffins and pyridine. The mixture is now washed five times with water, the benzole layer dried with calcium chloride and the sp. gr. determined. The percentage of carbon disulphide is found by referring the two sp. gr. to Graph 2 (B).

If the carbon disulphide content of the sample is much above 15 per cent. the extraction with alcoholic alkali presents practical difficulty. Accordingly, if the original sp. gr. does not fall within the scope of the graph, the sample must be diluted with a sufficient proportion of pure benzene to reduce the sp. gr. to a suitable figure. The percentage of carbon disulphide found in the diluted sample is then corrected for the proportion of pure benzene added. Hoffert and Claxton[2] state that with crude benzoles they prefer to treat with alcoholic caustic potash before the unsaturated hydrocarbons are removed.

(c) *Paraffins including Naphthenes.* The sp. gr. of the paraffins (including naphthenes) in the fraction up to 90° may be taken as 0·700. If the percentage of paraffins lies outside the scope of the main graph, the sp. gr. of a paraffin-free benzene-toluene mixture of the ascertained toluene percentage is read from the table given below and the difference between this and the sp. gr. of the carbon disulphide-free sample is referred to Graph 2 (C).

Distillate below 90°. (ml.)	Specific gravity of equivalent benzene-toluene mixture.
98	0·8840
96	0·8830
94	0·8820
92	0·8810
90	0·8800

[1] *J. Soc. Chem. Ind.*, 1916, **35**, 911.
[2] *Motor Benzole, Its Production and Use,* London, 1931, p. 593.

When the percentage of carbon disulphide is above 15, the true paraffin content is obtained by multiplying the observed percentage by $\frac{100 - x}{100}$, where x is the percentage of carbon disulphide present. If the percentage of carbon disulphide is below 15, the correction need not be calculated since it can be read from the graph itself.

(d) *Benzene.* The benzene content is obtained by difference. In order to avoid lengthy description of the use of the graph the two following examples are given :—

Example I.

Mixture taken—

Toluene	4 per cent. by volume
Paraffin	3 ,, ,, ,,
Carbon disulphide . . .	12 ,, ,, ,,
Benzene	81 ,, ,, ,,
	100 per cent. by volume

Distillation of 100 ml. up to 90° gave 97·5 ml., indicating 3·6 per cent. toluene. The sp. gr. after the removal of the carbon disulphide was 0·8762. The junction of the 3·6 per cent. toluene and the sp. gr. 0·8762 lines is at 4·3 per cent. paraffins. The sp. gr. of the original sample was 0·9205, and the sp. gr. after removal of carbon disulphide was 0·8762, these figures corresponding to 12·5 per cent. carbon disulphide. In order to obtain the corrected value for the paraffins, the point representing the observed percentage is moved upwards continuously, equidistant from the continuous and then discontinuous straight lines, until it reaches a point representing the carbon disulphide percentage. This point gives the corrected value of 3·8 per cent. paraffins.

Example II.

Mixture taken—

Toluene	4 per cent. by volume
Paraffin	11 ,, ,, ,,
Carbon disulphide . . .	50 ,, ,, ,,
Benzene	35 ,, ,, ,,
	100 per cent. by volume

Distillation of 100 ml. up to 90° gave 97·1 ml., indicating 4 per cent. toluene. As the sp. gr. of the mixture was 1·0496 which is outside the graph, exactly 15 ml. were diluted five times, *i.e.* to 75 ml. with pure benzene; the sp. gr. of this mixture was 0·9150, and the sp. gr. after removal of carbon disulphide was 0·8794, indicating 10 per cent. of carbon disulphide in the diluted mixture, or $5 \times 10 = 50$ per cent. of carbon disulphide in the original sample. The junction of the 4 per cent. toluene and the 0·8794 lines is at 2·6 per cent. paraffin ; this figure, corrected as before, indicates 2·3 per cent. paraffins in the diluted mixture, or $5 \times 2{\cdot}3 = 11{\cdot}5$ per cent. in the original sample. For higher percentages of carbon disulphide and paraffins the results will be less accurate than those obtained in the

analysis of benzoles, but at the same time, there are no serious deviations from the true values. The results obtained usually fall within the following limits of the true figures :—

Toluene	$\pm$ 0·5 unit.
Paraffins	$\pm$ 1·0 ,,
Carbon disulphide . . .	$\pm$ 0·5 ,,
Benzene	$\pm$ 1·0 ,,

3. **Examination of Crude Benzole.**—A resumé of the testing provisions in *Standard Methods* for crude benzole is given below. The tests are applicable to crude benzole as defined (p. 164), to crude low-temperature spirit, and to crude light products from tar distillation and having a distillation range similar to that of crude benzole. The application of the tests to products containing substantial amounts of paraffins must, however, be made with circumspection and a full appreciation of the limitations which may then have to be set on the interpretation of the test results.

Any *separated water* is first removed and its quantity noted ; the tests are carried out on the remaining spirit. As in the case of light and middle oils, the tests may be grouped into preliminary tests and a commercial analysis, the analyst deciding whether the latter is to be carried out, depending on whether his examination of the sample is intended primarily for identification or evaluation.

The *sp. gr.* or *density* is of course first determined ; one or other of the recognized methods is used and the result reported on the basis of $S_{15 \cdot 5° C./15 \cdot 5° C.}$ or $\rho_{20° C.}$, as the case may be.

In *distillation* tests, it is still the custom in Great Britain to distil 100 ml. of the sample in a retort, with the bulb of the thermometer in the liquid, the principal cut-point being 120° C. as a stop-point. Experts, however, consider that the retort test is unsatisfactory for assessing the value of a crude benzole and that view is increasingly appreciated by those concerned in the sale of the material. Probably in the near future the retort test will be forsaken in favour of the following fractionation method.

The apparatus is fully standardized ; it consists essentially of a bolt-head flask to which an 8-bulb pear column is fitted by means of a cork ; a thermometer is fitted in the top of the column, the side arm of the column being attached to a Liebig condenser. The column must not be lagged. The flask is supported by a clamp at the neck, and not from the bottom. A Bunsen burner flame is applied directly to the bottom of the flask, with no intervening gauze or asbestos.

The test is carried out on 100 ml. of the sample, but, in order that distillation of the sample may proceed as far as possible, 20 ml. of a prepared creosote oil is added to the 100 ml. of sample. This added creosote oil is prepared by fractionating phenols-free creosote oil

through an 8-bulb column to 190° C. and taking the 20 ml. from the liquid portion resulting from the cooling of the residue in the flask to 15·5° C. for two hours.

A 100 ml. Crow receiver is used to collect the distillate resulting from the fractionation of the mixture of sample and prepared creosote oil, the rate of distillation being 5 ml. per minute (about two drops per second), stop-points and/or running-points being taken as required.

If water accumulates during the process, the test is started afresh on a portion of the sample previously dried over plaster of Paris with which it has been shaken for ten minutes. The test report must indicate if such preliminary drying has been done and allowance for the water removed must be made in the calculation of the results, the amount of water present being determined separately.

The *total sulphur* and the *carbon disulphide* contents are usually required, generally the amounts in the fraction to 160° C. If so, the distillate to that temperature in the fractionation test above described is shaken for half a minute with 10 per cent. by volume of 10 per cent. caustic soda solution and portions of the washed fraction subjected to the tests described later for total sulphur and for carbon disulphide in refined lower boiling products (see pp. 262 and 274).

The *commercial analysis* comprises a determination of the loss on acid-washing and the determination of the contents of either commercial fractions or pure products in the acid-washed material.

Loss on acid-washing is determined on lines closely similar to that outlined on p. 181. In respect of light and middle oils examination it should be observed that that treatment represents drastic acid-washing conditions and is intended to be correlated with the manufacture of pure products. The sample will usually be sufficiently clean to permit of acid-washing directly ; if, however, it contains more than 10 per cent. of material distilling above 190° C., troubles will arise in the acid-washing procedure ; in such cases, 500 ml. of the sample is fractionated through the standard 8-bulb pear column and the distillate to 190° C. is used for the subsequent acid-washing test (no creosote oil need be added in the fractionation just mentioned, of course, as the treatment will only be carried out on samples containing sufficient heavy material to ensure that the distillation temperature of 190° C. will be reached).

Further pre-treatment is required as follows : (*a*) for the removal of phenols and hydrogen sulphide, by washing with sufficient 10 per cent. caustic soda solution ; (*b*) for the removal of pyridine bases, by washing the phenols-free material with 25 per cent. sulphuric acid. These washings are given, of course, whether the original sample or the fraction to 190° C. is being used for the acid-washing test.

Standard Methods requires that, if the acid-washed material is to be examined for pure products, it must give a negative result in a prescribed test for unsaturated hydrocarbons which might have survived the acid treatment.

If the contents of *pure products* are required, the acid-washed material is now subjected to the Colman and Yeoman test (assuming that the washed material qualifies for such examination—see preceding paragraph). The results available from the commercial analysis will then be :—

Carbon disulphide	Xylene
Paraffins	Heavy naphtha
Benzene	Loss on acid-washing
Toluene	Wash oil or creosote oil

the last mentioned being the residue in the fractionation process of the Colman and Yeoman test plus the residue in the fractionation preliminary to the acid-washing test, if that preliminary fractionation had to be carried out.

Alternatively it may be desired to know the amounts of *commercial fractions* in the acid-washed material. The acid-washed material is then fractionated in prescribed apparatus consisting essentially of a bolt-head flask of suitable size, an 8-bulb pear column, a Liebig condenser, a thermometer having an appropriate range and a number of graduated receivers of appropriate capacities.

Fractions are taken, at a distillation rate of 4 to 5 ml. per minute, as follows :—

Up to 100° C.	Commercial benzole
100° ,, 120° C.	Commercial toluole
120° ,, 160° C.	Solvent naphtha
160° ,, 190° C.	Heavy naphtha

each temperature being a running-point except the last, which is a stop-point, and all temperatures being corrected for atmospheric pressure, etc. The yields give an approximation to the available contents of the products indicated; the sp. gr. of the fractions give some indication of their respective paraffins contents. The fractions may, if desired, be examined by the methods prescribed for refined lower boiling products (see p. 207 *et seq.*). The following are reported as percentages by volume on the original sample freed from any separated water :—

Commercial benzole	Heavy naphtha
Commercial toluole	Loss on acid-washing
Solvent naphtha	Wash oil or creosote oil

the last mentioned being the residue in the foregoing fractionation

plus the residue in the fractionation preliminary to the acid-washing test, if that preliminary fractionation had to be carried out.

Standard Methods gives details of adjustments to be made in the event of material amounts of water collecting in the fractionation for commercial fractions, the adjustments being based on the assumption that such water represents unrecorded acid-washing loss. The oil coming over with such water is added back to the flask and the fractionation process resumed.

Standard Methods for the examination of crude benzoles assume normal samples and results normally required in commercial practice. Phenols and pyridine bases are not usually present in commercially significant quantities and are not specifically determined, nor is it necessary normally to determine ammonia. The following notes on available methods are given for guidance when special circumstances demand determinations of these materials :—

(a) *Phenols.* Phenols in crude benzole may be rapidly estimated by the method of Colman and Yeoman,[1] a slight modification of which is thus described by Hoffert and Claxton [2]: 100 ml. of the crude benzole is shaken for five minutes with 25 per cent. by volume of 10 per cent. sodium hydroxide solution in a wide graduated burette provided at the top with a bulb, 75 mm. in diameter and fitted with a ground glass stopper. The diameter of the burette is 23 mm. and the burette is graduated from 0 to 100 ml. in ml. After settling, the alkali is run off, the benzole washed with water and allowed to settle. The percentage diminution in volume is stated as the tar-acids content of the benzole. The results so obtained are only approximate, and if an accurate determination is required the following method may be employed :—

100 ml. of the sample is shaken vigorously in a 250 ml. glass flask with 25 ml. of 10 per cent. aqueous sodium hydroxide solution for five minutes. The alkali is measured in the cylinder from which the 100 ml. of the sample has been emptied. If it contains naphthalene, the sample and the sodium hydroxide solution must be warmed to about 40° before mixing. The washed oil is then recovered, using a separating funnel, and then agitated with a further 25 ml. of the sodium hydroxide solution for five minutes, and with further successive washings of the same quantity of sodium hydroxide solution until all the phenols have been removed. The combined soda washings are boiled for ten minutes or until the odours of tar oils and bases have disappeared, cooled to atmospheric temperature and poured into a special standard phenols flask (p. 439). The washings are now acidified with concentrated hydrochloric acid solution, using methyl

[1] *J. Soc. Chem. Ind.*, 1919, **38**, 57 T.
[2] *Rept. Joint Benzole Res. Comm.*, 1926, p. 37.

orange as indicator. The acidity must persist after vigorous agitation of the two layers. The aqueous layer is saturated with 25 g. of powdered sodium chloride, the phenols brought into the graduated neck by adding saturated salt solution and, after settling overnight, the volume of phenols is read off. With samples rich in phenols a smaller quantity of the sample must be treated to bring the liberated phenols within the graduated portion of the neck of the flask.

(b) *Tar Bases.* 100 ml. of the sample, freed from phenols as described above, is agitated in a separating funnel with 30 ml. of sulphuric acid solution containing 25 parts per 100 by weight of H_2SO_4, and, after settling, the acid layer is drawn off into a flask of 500 ml. capacity. The residual benzole is washed with water, the washings run into the same flask, and 50 ml. of 16 per cent. aqueous sodium hydroxide solution added, the mixture being cooled the while. The alkaline sodium sulphate solution is steam distilled, the distillate being collected, through an air condenser, in a 250 ml. titration flask containing 100 ml. of $N/2$ sulphuric or hydrochloric acid to which a few drops of methyl orange have been added. Active steam distillation must continue for a period of twenty minutes, and if the temperature of the acid solution has increased appreciably, it must be cooled to laboratory temperature before titration with $N/2$ aqueous sodium hydroxide solution (free from carbonate). In the absence of ammonia, the difference between 100 ml. and the number of ml. of $N/2$ sodium hydroxide solution required for neutralization, multiplied by 0·0395, represents the percentage of bases expressed as pyridine. This figure will include any ammonia, which may be determined as below.

(c) *Ammonia.* If ammonia is present it must be determined on the bases from a separate steam distillation of the alkaline sodium sulphate solution into an empty receiver. The limits of accuracy of this test are stated to be $\pm$ 10 per cent. of the true value. For the estimation of the ammonia a suitable amount of the bases is weighed accurately, dissolved in distilled water and made up to 250 ml. 50 ml. or a suitable aliquot part of this solution is titrated with $N/10$ sulphuric acid, using 0·5 ml. of thymol blue (0·04 per cent. in 60 per cent. alcohol) as indicator, until first the blue and then the green colour disappears and the final yellow colour matches that of a prepared standard. The amount of ammonia in the sample is then calculated, 1 ml. of $N/10$ sulphuric acid being equivalent to 0·0017 g. of ammonia (NH_3).

The colour standard is prepared by titrating 25 ml. of approximately $N/10$ ammonia with $N/10$ sulphuric acid, using methyl orange as indicator. Another 25 ml. of the ammonia solution is then neutralized exactly by adding an amount of acid equal to that required in the

first titration; 0·5 ml. of the thymol blue indicator is added, together with pure pyridine, the amount of the latter being approximately that which is used in the actual determination. No appreciable colour change is usually noted on addition of the pure pyridine. The whole is then diluted with distilled water to the volume (about 75 ml.) used in the titration of the sample, and transferred, if necessary, to a vessel similar to that in which the titration of the sample is performed. This method is the Standard Method for the estimation of ammonia in tar bases.[1]

(d) *Unsaturated Hydrocarbons.* One of two methods is generally applied for the estimation of unsaturated hydrocarbons: (*a*) treatment with concentrated sulphuric acid, effecting polymerization and solution of the unsaturated hydrocarbons, or (*b*) treatment with bromine, iodine or oxygen in order to express unsaturatedness in terms of the equivalent value of one of these elements. Proposed methods have been examined by Manning and Shepherd.[2] Commercial testing has developed on the basis of both the above-mentioned principles, and "loss on acid-washing" and "bromine absorption" both figure in commercial specifications.

(1) *Treatment with Sulphuric Acid.* The Standard Method for acid treatment has already been described (see p. 181); some mention of the investigatory work behind the modern Standard Method is desirable. Sulphuric acid of lower strength than 80 to 87 per cent. does not completely remove the unsaturated hydrocarbons, and 87 per cent. acid is stated to attack the aromatic hydrocarbons. According to Faragher, Gruse and F. H. Garner,[3] however, sulphuric acid of lower strength than 95 to 98 per cent. may not completely remove the unsaturated hydrocarbons and there is the possibility of the formation of dipolymers still containing one double bond. Compounds such as pentenes and hexenes, according to the conditions, may form alcohols and paraffins which redissolve in the benzole.[4] Hoffert and Claxton[5] state that the unsaturated hydrocarbons are only completely removed with relatively large amounts of 95 per cent. sulphuric acid, which, however, attacks benzene and its homologues, and that, apparently, there is no strength of acid which removes the unsaturated hydrocarbons without attacking the saturated hydrocarbons. With 50 per cent. by volume of 90 per cent. acid the resulting reduction in volume of the benzole is less

[1] Communicated by T. Callan.

[2] *Fuel Research Board*, Technical Paper No. 28, 1930.

[3] *Ind. Eng. Chem.*, 1921, 13, 1044.

[4] Michael and Brunel, *Amer. Chem. J.*, 1909, 41, 118; Ormandy and Craven, *J. Soc. Chem. Ind.*, 1928, 47, 317 T; 1929, 48, 293 T; J. F. Norris and H. S. Davis, *J. Soc. Chem. Ind.*, 1929, 48, 70 T.

[5] *Motor Benzole, Its Production and Use*, London, 1931, p. 573; *Rept. Joint Benzole Res. Committee*, 1927, p. 198.

dependent on the exact quantity of acid used; with weaker acid there is a greater tendency to emulsification. The use of a mixture of sulphuric and boric acids, proposed by Kattwinkel [1] has been shown to fail.[2] Even if the treated material is distilled to the same end-boiling point as the original product (the amount of the residue being added to that of the unsaturated hydrocarbons), no means are available to determine the quantity of polymerized bodies boiling within the original distillation range.

A rapid empirical method, using sulphuric acid, is proposed by Hoffert and Claxton.[3] A measured quantity of the benzole (freed from tar phenols by the method described previously, and from pyridine bases by washing with 10 per cent. by volume of 30 per cent. sulphuric acid) is placed in the modified burette used in the tar phenols estimation. 5 per cent. by volume of 95 per cent. sulphuric acid is added and the mixture shaken for two minutes, cooling with water during this period. The burette is then allowed to stand in a vertical position for fifteen minutes, the acid layer thereafter drawn off slowly and water carefully run down the sides of the burette without shaking. The acid tar is completely removed with a second water wash, followed by a wash with 10 per cent. by volume of 5 per cent. sodium hydroxide solution. The loss in volume expressed on 100 ml. of the benzole represents the percentage content of unsaturated hydrocarbons.

(2) *Bromine Absorption.* The quantity of bromine absorbed is not a satisfactory measure of the unsaturation of an oil since unsaturated hydrocarbons of unknown molecular weight may be present in the material examined and substitution as well as saturation of the molecule at the double bond may take place.

Ease of substitution is dependent on molecular structure,[4] but substitution is minimized if excess of bromine is avoided, as in the bromide-bromate method of Kraemer and Spilker.[5] A standard solution of potassium bromide and potassium bromate is shaken with an aliquot amount of the sample under examination; standard sulphuric acid solution is added to free the bromine for saturation as required.

Standard Methods prescribes the bromine absorption method for the determination of unsaturated hydrocarbons; the procedure is outlined below:—

0·5 *N.* bromide-bromate solution and approximately 0·2 *N.* sodium thiosulphate solution are required. The latter is standardized

[1] *Brennstoff-Chem.*, 1927, **8**, 353.

[2] Tropsch and Koch, *Brennstoff-Chem.*, 1929, **10**, 337.

[3] *Loc. cit.*, p. 575; *cf.* Colman and Yeoman, *J. Soc. Chem. Ind.*, 1919, **38**, 57 T.

[4] Faragher, Gruse and F. H. Garner, *loc. cit.*

[5] Lunge, *Coal Tar and Ammonia*, London, 5th edn., 1916, p. 978; Williams, *Rept. Joint Benzole Res. Comm.*, 1924, p. 127.

immediately before use by means of the 0·5 *N.* bromide-bromate solution. The Standard Method should be followed for this titration and, later, in the actual determination of the unsaturated hydrocarbons. 5 ml. of the bromide-bromate solution and 10 ml. of fresh 10 per cent. potassium iodide solution are placed in a glass-stoppered bottle with 20 ml. of 10 per cent. sulphuric acid. The stoppered bottle is thoroughly shaken, the liberated iodine titrated with the sodium thiosulphate solution until the mixture is faintly yellow, when starch solution is added and the titration completed.

For the determination of unsaturated hydrocarbons, 20 ml. of the sample, 5 ml. of 10 per cent. sulphuric acid and sufficient of the bromide-bromate solution to produce a distinct yellow in the sample layer after vigorous shaking for one minute, are shaken in the stoppered bottle for that period. An excess of bromide-bromate solution must be avoided and a reddish-yellow colour persisting after the shaking will demand that the test be started afresh.

The bromine is completely liberated by adding 15 ml. of 10 per cent. sulphuric acid and shaking for another minute. A little more bromide-bromate solution must be added if necessary to retain the distinct yellow colour. Throughout all the shaking the bottle is wrapped in dark material to minimize the action of light.

The excess of bromine is determined by the addition of potassium iodide solution, and titration with the sodium thiosulphate solution; the back titre must be between 0·5 and 1·5 ml. The bromine absorption figure is $0{\cdot}40\,(0{\cdot}5\ V_1 - nV_2)$, where V_1 and V_2 are the volumes of bromide-bromate solution and sodium thiosulphate solution used respectively, and n is the factor for the sodium thiosulphate solution. Francis [1] states that errors due to substitution and caused by the rapid generation of bromine in high concentrations, may be minimized by the following procedure which gives consistent results :—

An aqueous *N*/2 bromide-bromate solution is prepared containing 49·5835 g. of potassium bromide and 13·9175 g. of potassium bromate per litre. A measured quantity of the sample, together with 5 ml. of 10 per cent. aqueous sulphuric acid, is shaken in a stoppered bottle with such a quantity of the *N*/2 bromide-bromate solution as will cause the sample to remain a faint yellow colour after one minute's shaking. A further 15 ml. of acid is now added to complete the liberation of the bromine and shaking continued for one minute. If the sample is then colourless, sufficient bromide-bromate solution is added to cause the faint yellow colour to persist. Excess of bromine is now determined by the addition of a few ml. of a 10 per cent. aqueous potassium iodide solution and titration with *N*/5 sodium thiosulphate solution, previously standardized against the bromide-

[1] *Ind. Eng. Chem.*, 1926, **18**, 821.

bromate solution, using a starch solution as indicator. If T and N represent the titration and normality of the bromide-bromate solution, t and n the titration and normality of the thiosulphate solution, and D and V the density and volume of the sample respectively, then

$$0{\cdot}08 \frac{(TN-tn)}{VD} = \text{g. of bromine per gram. of the sample.}$$

If the actual percentage of unsaturated hydrocarbons is required, this may be obtained by assuming that M, the mean molecular weight of the olefines is, for a narrow cut of distillate, approximately 54 plus half the mean boiling point in ° C., a relation based upon the boiling points of the pure normal olefines. The percentage of unsaturated hydrocarbons then equals MN/160 where N equals the bromine number calculated as above.

Other tests applicable to crude benzole are described in the appropriate section dealing with refined products.

(*c*) The Working up of Crude Naphtha, Crude Benzole and Light Oil

The tar phenols in crude naphtha are removed before or after redistillation dependent upon works conditions. The crude naphtha yields a crude benzole and a crude solvent fraction, the change over being made as soon as the fraction on laboratory distillation shows the first drop at 110°, the second fraction ending when the sp. gr. of the distillate is from 0·965 to 0·970 at 60° F. Alternatively, the change over points may be determined by temperature, these varying according to market requirements. The residue may be worked up with light oil. Rectification of the crude naphtha yields principally 50/90's benzole and 90's benzole. The former in a retort distillation test yields 50 per cent. by volume at 100° and 90 per cent. at 120°; the latter yields 90 per cent. by volume between 80° and 100°. Crude benzole recovered by oil washing approximates to 65's crude benzole, that is to say, 65 per cent. by volume up to 120° in the retort test, corresponding to a yield of 75 per cent. at 120° when the vapour temperature is taken. The further working up of the crude benzole consists of repeated washings with sodium hydroxide and with strong sulphuric acid, followed by rectification with a dephlegmating column. In the rectification process the forerunnings up to 80° may be treated separately, since it is in this portion that the carbon disulphide is concentrated and the fraction also contains large amounts of low-boiling unsaturated hydrocarbons. The sulphur in the remaining fractions is due chiefly to thiophen and its derivatives, whilst large amounts of unsaturated hydrocarbons are also present in the highest fractions of the crude benzole.

Separate treatment of the forerunnings and the highest boiling fractions thus requires a smaller amount of reagent and in the preparation of motor benzole, a smaller loss of unsaturated hydrocarbons results. To avoid excessive loss of unsaturated and polymerizable bodies in the refining and fractionation of the crude benzole for motor benzole, an alternative procedure may be adopted. With some benzoles it suffices to remove the tar phenols and pyridine bases, to redistil and then to add small amounts of bodies termed inhibitors to prevent resinification of the finished product on storage. The inhibitors employed may be cresols, pyrogallol, α-naphthol or *p*-methylaminophenol.[1] Another method is to use an acid ferric sulphate preparation to effect partial removal of the unsaturated constituents.[2] The control of the working conditions extends chiefly to testing the purity of the washed benzoles—*i.e.* their distillation range, and, in acid-washed products, their behaviour to concentrated sulphuric acid and to bromine as described previously. According to the result of these latter tests the washing process is continued until the washed product corresponds to the standard of purity required. The yield of final products is determined by careful distillation under standard conditions.

Light oil is generally washed free from tar phenols and bases before redistillation to produce intermediate products which vary according to the final products required. Commonly a crude benzole-toluole fraction, an intermediate fraction to be redistilled, a crude solvent naphtha fraction and a heavy naphtha fraction are recovered. The crude benzole-toluole fraction may be re-fractionated to produce a crude benzole, an intermediate fraction for redistillation and a crude toluole fraction. The benzole and toluole fractions may be subjected to washing with concentrated sulphuric acid, followed by a weak alkali wash, and then fractionally distilled to give a product of the required boiling range. In a similar way refined solvent naphthas and refined heavy naphthas are produced to comply with specification requirements.

II. CRUDE CARBOLIC AND CRESYLIC ACIDS

Crude carbolic and cresylic acids are extracted from the crude naphtha, light oil, and light creosote by washing with sodium hydroxide solution either before or after redistillation. Sometimes only a portion of the tar phenols may be removed before redistillation ; the remainder is recovered by washing the fractions from the redistillation. The crude tar phenols are recovered by acidifying the wash liquors with

[1] Hoffert and Claxton, *J. Soc. Chem. Ind.*, 1933, 52, 25 T.

[2] Cox and M'Dermott, B.P. 269242 ; Hart, Harris, Hart and Co., Ltd., and Refiners, Ltd., B.P. 278883, 1926.

carbon dioxide or with sulphuric acid solution. In either case an interchange may be effected between the carbolic acid in an oil rich in carbolic acid and the cresylic acid in phenolate wash liquor rich in cresylic acid, the carbolic acid combining with the soda and the cresylic acid going into solution in the oil. An oil containing a fair amount of naphthalene will deposit naphthalene freely after the tar phenols have been washed out, as the tar phenols appear to assist in keeping the naphthalene in solution. Crude carbolic acids are manufactured only from those phenolates which contain crystallizable tar phenols. Cresylic acids are manufactured from those phenolates which contain tar phenols which do not crystallize at about 35° F. and generally from the last wash of the light oils and all the washes but the first of the light creosotes. The works control tests in these operations comprise chiefly the determination of the tar phenols to ascertain the strength and amount of sodium hydroxide or phenolate solution required in the washing processes. As washing proceeds the crystallizing points of the treated oils may be required.

(a) The Examination of Crude Carbolic and Cresylic Acids

(1) **General.**—The *sp. gr. or density* may be determined by any of the recognized Standard Methods. The temperature corrections are given on p. 130.

The Standard Method for *distillation* of the crude acids is carried out in a standard distillation flask of 130 ml. distillation capacity, fitted with a suitable standard thermometer and air condenser. A British standard draught-screen is used with a sheet of wire gauze between the flask and the flame of a Bunsen burner which is used as the source of heat. A standard wide-mouthed unstoppered Crow receiver is used to collect the distillate.

The test is performed on 100 ml. of sample under normal standard conditions. The distillation is slow until all water has come over and is thereafter increased to 3·0 to 3·5 ml. per minute. The Standard Method recommends particular distillation points for recording. The basis for barometric corrections is given in the Standard Method.

The chief impurities to be expected in samples of crude carbolic and cresylic acids are *neutral oils* and *pyridine bases*. For their determination, a 500 ml. round-bottomed flask is connected through a spray trap with a standard Liebig condenser (see Fig. 34). 50 ml. of the sample, 85 ml. of 27 per cent. caustic soda solution and 100 ml. of water are thoroughly mixed in the flask, the apparatus assembled and the contents of the flask distilled as rapidly as is compatible with complete condensation.

Precautions must be taken in the event of the sample being relatively rich in naphthalene, both to avoid solidification in the condenser or

loss of naphthalene by volatilization. The distillate is collected in a specially designed receiver consisting of a pear-shaped body with a lower graduated tube finishing in a stopcock ; 100 ml. of condensate is collected.

The receiver is warmed if necessary and just sufficiently to liquefy any solid portion of the contents. It is then set vertically, the contents allowed to separate completely, the aqueous solution run into a titration flask, and the volume of the neutral oils remaining in the graduated

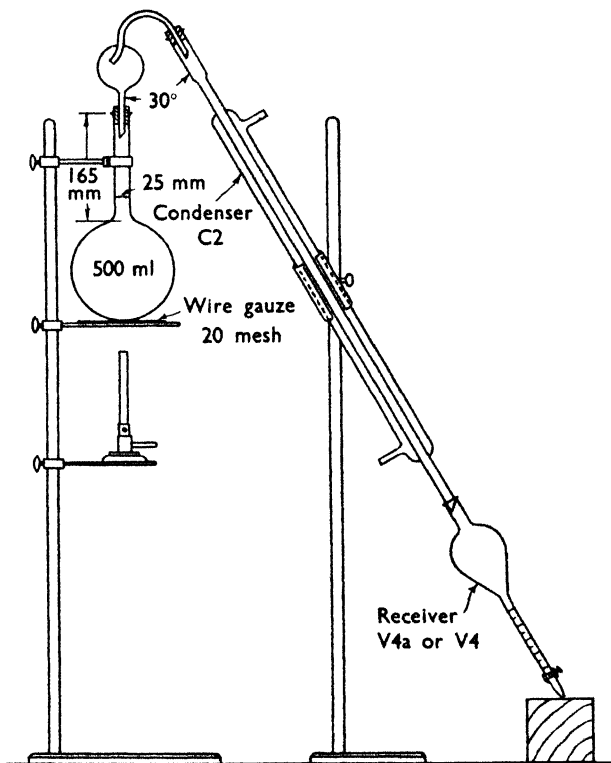



FIG. 34.—Neutral Oils and Pyridine Bases in Carbolic and Cresylic Acids—Assembled Apparatus

portion of the receiver is noted. Twice this volume is the percentage of neutral oils, as 50 ml. of sample was taken for test.

The remaining contents of the receiver are run into the titration flask and the washings from two successive washings of the funnel with two successive quantities of 10 ml. of distilled water are added to the titration flask. The contents of this flask are made neutral to phenolphthalein by the cautious addition of 0·1 *N.* hydrochloric acid and are then titrated against *N.* hydrochloric acid until neutral to methyl orange.

The *N.* hydrochloric acid titre, multiplied by 0·158, represents the percentage of pyridine bases expressed as pyridine.

Modifications of the Standard procedure are prescribed for samples containing either excessive or especially limited amounts of neutral oils and pyridine bases, and for samples which yield a distillate which does not readily separate.

The remaining test which is applied equally to carbolic and cresylic acids is that for *acidity or alkalinity*, as the case may be. These are determined respectively in terms of sulphuric acid and sodium hydroxide. Phenol red indicator solution, to a prescribed formula, is used in the Standard Method, which starts with a preliminary determination whether the sample is acid or alkaline, by adding a drop of the sample to three drops of the indicator solution on a white porcelain tile.

100 ml. of the sample is then titrated with *N.* sodium hydroxide or hydrochloric acid solution, according as the sample has been found to have an acid or an alkaline reaction. The phenol red is used as an external indicator. The titre, multiplied by 0·049 for acid samples, or 0·04 for alkaline samples, gives the percentage of acidity or alkalinity recorded on the basis previously mentioned.

(2) **Crude Carbolic Acid.**—The commercial examination of crude carbolic acid involves the determination of water and of residue on distillation, and the carrying out of the Lowe's test. The original Lowe's test was modified by Graesser and in the form evolved in *Standard Methods* is now the universally accepted technique. The test is empirical and requires to be carried out with the greatest care and the strictest adherence to detail if comparable results are to be expected. The original text of the Standard Method must be consulted in such circumstances. The tests for water and residue are carried out in train with the preparation of that portion of the distillate of the sample required for the Lowe's test. It is difficult to define the applicability of the test and experience alone will decide the limit to which it may be applied ; the method is only applicable to material which, by the test, gives a Lowe's test figure between 45° and 80° F.

The first part of the Standard Method is a distillation procedure. A standard distillation flask of 130 ml. distillation capacity is fitted with a standard thermometer reading from 150° to 250° C. and an air condenser which is specific in design for the present test. The flask is protected from draughts by a British standard draught-screen in which the normal asbestos sheet is replaced by wire gauze. One of each of the three sizes of standard Crow receivers are required, that of the largest size (100 ml.) being stoppered. Heating is effected by means of a Bunsen burner. All the apparatus must be scrupulously clean and thoroughly dried. 100 ml. of the sample is measured into the flask and the distillation started at the rate of one drop in five to six seconds. The 50 ml. receiver is used to collect the

distillate until all water has come over and thereafter until 10 ml. of clear distillate has collected.

The 50 ml. receiver is then replaced by the 100 ml. receiver and the distillation rate increased to one drop per second, at which rate it is maintained until 62·5 ml. of distillate has collected in that receiver. That receiver is then replaced by the 25 ml. receiver and the distillation continued to the pitching point.

The amount of residue is obtained by weighing; if it does not exceed 2 g., the sample is reported as free from residue. (This allowance

± 5 per cent. tolerance on dimensions except where otherwise stated. All diameter dimensions are external.

FIG. 35.—Crystallizing point—Assembled Apparatus.

is regarded as the amount of hold-up in the flask—*i.e.* the amount which cannot be distilled over from a sample which is free from residue.)

The volume of aqueous distillate in the 50 ml. receiver is measured at the end of the distillation; this receiver must naturally not have been shaken at any stage.

The remainder of the technique consists of the determination of the crystallizing point of the 62·5 ml. fraction in the 100 ml. receiver. For this purpose, the contents of that receiver are thoroughly mixed by shaking and about 20 ml. is placed in the inner tube of the standard crystallizing point apparatus (Fig. 35). The apparatus is fitted with

a standard thermometer covering the range 40° to 85° F. and the assembled apparatus is placed in a bath not more than 3° F. below the expected crystallizing-point. When the contents of the inner tube have cooled to about 0·5° F. above the expected crystallizing point (ascertained roughly on a separate portion of the distillate), the cooling sample is seeded with a small crystal of phenol. The cooling is continued with constant stirring until the sample is crystallized throughout, the highest temperature recorded after crystallization commences being the crystallizing point which is recorded. Various precautions and annotations to the method appear in *Standard Methods*.

For good crude carbolic acid the " Lowe's Test " should lie between 15·5° and 24°. For comparison, standard mixtures of pure crystallized carbolic acid and cresol (preferably tar-cresol, a mixture of the three isomers) are used, the crystallizing points of which have previously been determined. Mixtures of phenol with pure *o*-, *m*- and *p*-cresol cannot be used, as Lunge [1] has pointed out, since coal tar cresol contains all three isomers, and the proportions of the isomers in cresols from different sources are not identical.

(3) **Crude Cresylic Acid.**—The *commercial examination* of crude cresylic acid consists in the determination of the *water and phenol contents* and the determination of the *residue on distillation*. Strictly speaking, the method is only applicable when neutral oils and tar bases are absent, but for practical purposes may be used if the total amount of these substances does not exceed 3 per cent. It is applied when a sample which would have a Lowe's test result below 45° F. is submitted for commercial evaluation.

In the Standard Method two round-bottomed flasks, of specified dimensions and bulb capacities approximating to 850 ml. and 350 ml. respectively, are required. At the outset of the test the 850 ml. flask is fitted with a standard 12-bulb pear column ; a standard thermometer (150° to 250° C.) is fitted at the top of the column, the side arm of the column being connected to a standard air condenser. The flask rests on wire gauze, a Bunsen burner is used as the source of heat, and a cylindrical screen, of a height so specified that the flask and column are protected from draughts, is employed.

250 g. of the sample is weighed into the flask, the apparatus assembled with the column vertical and the contents of the flask distilled slowly to 170° C., a 50 ml. stoppered Crow receiver being used to collect the distillate. The phenols in the distillate are salted out with just sufficient powdered sodium chloride to saturate the aqueous layer and leave a few particles undissolved. The volume of the aqueous layer, multiplied by 0·9, is recorded as the water content

[1] *Coal Tar and Ammonia*, London, 5th edn., 1916, pp. 277, 788.

of the amount of sample examined, whence the percentage water content can be calculated.

The phenols in the distillate to 170° C. are returned to the 800 ml. flask when the latter has cooled to about 100° C., and the distillation is resumed at the rate of 3·0 to 3·5 ml. per minute, fractions being taken (*a*) up to 195° C. and (*b*) between 195° and 205° C., the former being a running-point and the latter a stop-point. The first fraction is collected in a weighed conical flask (250 ml. size) and the second fraction in the 350 ml. round-bottomed flask.

Relation between Crystallizing Point and Phenol Content

Crystallizing point °C.	0·0.	0·1.	0·2.	0·3.	0·4.	0·5.	0·6.	0·7.	0·8.	0·9.
	Fractional Phenol Content by Weight.									
27	0·757	0·759	0·760	0·762	0·764	0·766	0·767	0·769	0·771	0·773
28	0·774	0·776	0·778	0·780	0·781	0·783	0·785	0·787	0·788	0·790
29	0·792	0·794	0·795	0·797	0·799	0·801	0·802	0·804	0·806	0·808
30	0·809	0·811	0·813	0·815	0·816	0·818	0·819	0·821	0·823	0·825
31	0·826	0·828	0·830	0·832	0·833	0·835	0·837	0·839	0·840	0·842
32	0·844	0·846	0·847	0·849	0·851	0·853	0·854	0·856	0·858	0·860
33	0·861	0·863	0·865	0·867	0·868	0·870	0·872	0·874	0·875	0·877
34	0·878	0·880	0·882	0·884	0·885	0·887	0·889	0·891	0·892	0·894
35	0·896	0·898	0·899	0·901	0·903	0·905	0·906	0·908	0·910	0·912
36	0·913	0·915	0·917	0·919	0·920	0·922	0·924	0·926	0·927	0·929
37	0·931	0·933	0·934	0·936	0·937	0·939	0·941	0·943	0·944	0·946
38	0·948	0·950	0·951	0·953	0·955	0·957	0·958	0·960	0·962	0·964
39	0·965	0·967	0·969	0·971	0·972	0·974	0·976	0·978	0·979	0·981
40	0·983	0·985	0·986	0·988	0·989	0·991	0·993	0·995	0·996	0·998
41	1·000	...	...	...	...	...	...	...	...	...

The remainder of the contents of the 850 ml. flask is distilled to the pitching point, after the column has been removed and the flask (carrying a suitable thermometer and a glass bend) has been connected directly to the air condenser. The weight of residue is obtained by difference. If it does not exceed 5 g. the sample is reported to be free from residue ; otherwise the percentage by weight of residue is calculated and reported.

The fraction from 195° to 205° C. is redistilled from the flask in which it was collected, at the same rate and through the same column and condenser as was used in the preceding distillation. The distillate to 197° C. is collected in the conical flask already containing the fraction (*a*) up to 195° C. The combined distillate is thoroughly mixed and weighed, and about 20 g. is weighed accurately into a

standard distillation flask having a distillation capacity of 130 ml. An accurately weighed amount of 99/100 phenol is added, the amount being about four times the weight of distillate taken into the 130 ml. distillation flask. The neck of the flask is closed with a cork and the flask heated until 2 ml. of distillate has collected, the side arm of the flask acting as a condenser. The portion of the neck of the flask above the side arm is heated gently during the distillation to prevent condensation of water there. A calcium chloride tube is fitted to the side arm and the flask allowed to cool. The crystallizing point of the contents of the flask is determined by the Standard Method (see p. 325).

The fractional phenol content is ascertained by referring the crystallizing point to the table (page 203); the fractional phenol content of the 99/100 per cent. phenol is ascertained by a determination of its crystallizing point and reference to the same table.

The percentage by weight of phenol in the original sample is—

$$\frac{0{\cdot}4W_1(PW_2+PW_3-P_1W_3)}{W_2}$$

where

W_1 = the weight of the combined distillate fraction A and the distillate from fraction B up to 197° C.;
W_2 = the weight of the portion of this combined distillate used for the crystallizing point determination;
W_3 = the weight of the phenol added;
P = the fractional content of pure phenol in the mixture used for the crystallizing point determination; and
P_1 = the fractional content of pure phenol in the phenol added.

(*b*) The Working up of Crude Tar Phenols

Crude carbolic acid has a sp. gr. varying with its content of water from 1·05 to 1·065 at 15°, and is essentially a mixture of phenol with the three isomeric cresols and xylenol. Frequently the crude carbolic acid is sold as such, or it may be given a preliminary purification by washing, with the addition of a little sodium carbonate in order to remove mineral acids. Pure carbolic acid is manufactured by fractionation, the first fraction up to 180° consisting mainly of water, hydrocarbons and a small quantity of phenol which later is recovered; the second fraction between 180° and 205° is the principal fraction from which the phenol is obtained by crystallization. The third fraction from 205° to 220° contains principally the three cresols, and also considerable quantities of crystallizable phenol. The residue is either run to creosote or redistilled to yield liquid carbolic acid, that is, the cresols. The crude cresylic acids are, in like manner, fractionated to crude carbolic acid and to a large variety of commercial products which consist essentially of a mixture of the three isomeric cresols with

a little phenol and xylenols. Prior to marketing, the cresylic acid as obtained from the fractionating still has to be air-blown to remove objectionable sulphur compounds, which give the product an unpleasant odour. Crude cresylic acid is commonly sold on the basis of 95 per cent. or 97 to 99 per cent. of tar acids with a sp. gr. which generally varies between 1·042 to 1·055.

III. CREOSOTE OIL OR HEAVY OIL

(a) Properties.—Creosote oil is a semi-liquid product, having a characteristic smell which is unpleasant and almost nauseous, due probably to sulphur compounds; it distils between 200° and 300° and has an average sp. gr. (including about 20 per cent. of solid constituents) of 1·04.

(b) Composition.—The solid constituents comprise naphthalene, acenaphthene and allied hydrocarbons; the liquid constituents consist of from 8 to 10 per cent. of phenols (chiefly cresols and higher homologues), about 6 per cent. of pyridine bases and about 70 per cent. of hydrocarbons of unknown constitution, which await further investigation. Rispler[1] found about 28 per cent. of naphthalene and 16 per cent. of acidic compounds in creosote oil from gas tar and about 32 per cent. of naphthalene and 10 per cent. of acidic compounds in creosote oil from coke-oven tar.

(c) Methods of Examination.—The tests applied to creosote oil take into account the features of oils satisfactory for the main uses of creosote oil as such (as a preservative, principally of wood, or as a fuel oil) rather than the contents of individual chemical compounds in the oil. These tests are dealt with later under "Final Products" (see p. 359 *et seq.*).

If in the commercial distillation of crude tar, a marketable creosote oil is not collected directly, fractions are taken as follows:—

(*a*) Light creosote oil, distilling up to 230° C.
(*b*) Heavy creosote oil distilling up to 270° C.

The residue of the creosote oil fraction is worked up with the anthracene oil fraction if anthracene oil is being produced; otherwise it is added back to the heavy creosote oil and marketed as heavy creosote.

For further details as to the examination of creosote oils, see under "Final Products," p. 359 *et seq.*

(d) The Working up of Creosote Oil

Where light creosote oil has been separated it will probably be washed with sodium hydroxide solution to recover the tar phenols

[1] *Chem.-Ztg.*, 1910, **34**, 545.

(mainly cresols and higher homologues); the residue is either prepared to a required specification or added to the heavy creosote. Creosote oil and heavy oil are usually distilled or blended to meet buyers' requirements, there being numerous specifications for this purpose, all differing in some particular.

IV. ANTHRACENE OIL

(*a*) **Properties.**—This last fraction in the distillation of tar has a sp. gr. of 1·1 and boils between 280° and 400°; it has a greenish-yellow colour, which darkens gradually to greenish-brown and possesses a characteristic smell different from that of the other tar oils. Anthracene oil is liquid at 60°, but on cooling to the ordinary temperature separates from 6 to 10 per cent. of crude anthracene as a greenish-yellow powder containing from 25 to 30 per cent. of pure anthracene. In contrast to the other high-temperature tar oils it possesses a certain viscosity which renders it applicable as a lubricant for rough purposes.

(*b*) **Composition.**—Anthracene oil contains from 2·5 to 3·5 per cent. of pure anthracene; the other solid constituents include phenanthrene, carbazole, fluorene, acridine, etc. The proportion of phenols, for the most part of unknown constitution, is about 6 per cent. Comparatively little is known of the nature of the remaining constituents.

(*c*) **Methods of Examination** comprise the determination of the sp. gr., and of the boiling point and the estimation of the contained anthracene.

(*d*) The Working up of Anthracene Oil.

After the separation of the anthracene by allowing the oil to cool in open vessels, the solid constituents are removed, either by filtration or pressing. The oil thus separated is commonly worked up with the heavy creosote or may be employed, after treatment, as a wood preservative and the like; it may also be used as an absorbent for naphthalene in the manufacture of town's gas, a process originated by Bueb.

The residual crude anthracene is further dried either by pressing or centrifuging to remove adhering oil, when a product containing from 30 to 50 per cent. of pure anthracene is obtained, which is further purified by a variety of alternative processes up to a content of from 70 to 80 per cent. of pure anthracene.

V. PITCH

Coal tar pitch is considered as a final product (p. 409).

C. FINAL PRODUCTS

I. COMMERCIAL BENZOLES, TOLUOLES, XYLOLES, AND SOLVENT NAPHTHAS

(*a*) **Properties.**—Dependent on the nature of the crude material and on market requirements a wide range of products, in various states of quality and purity, is prepared from crude naphtha and light oil. Commercial benzole is used for very varied technical purposes. It is a valuable raw material in the organic chemical industry for the preparation of organic dyestuffs and pharmaceutical products and is also used in the manufacture of explosives. Nitration benzole and nitration toluole are closely refined products used respectively for the manufacture of nitrobenzole and nitrotoluole, benzyl chloride and other chemical derivatives where a high state of purity is essential. Both have a limited use as pure solvents. Nitration benzole contains small quantities of thiophen, and nitration toluole approximately an equal amount of thiotolen. Commercially pure benzole is also used as a solvent in the preparation of aircraft dope and protective covering.[1]

Owing to its marked solvent properties for fats, waxes, resins and essential oils, benzole, in common with the toluoles, xyloles and solvent naphthas is used in a large measure as an extraction agent. The most commonly used grade is that specified as 90's or 90 per cent. benzole, which is employed for such purposes as the production of mixed solvents ; for dry cleaning in competition with paraffin-base gasolines ; directly, as a solvent for resins, lacquers, oils, rubber cements, dyes (in the preparation of wood stains) and waxes ; for the extraction of bone, rosin and oils and for the degreasing of leather and hides. Although the distillation range is specified the composition may vary, periodically, with a varying demand for specific solvents. Thus, prior to the commencement of the lacquer industry, 90's benzole would contain approximately 75 per cent. of benzene, 23 per cent. of toluene and 2 per cent. of xylene. Toluole was then required in large quantities for this industry and accordingly 90's benzole specifications were met with a suitably proportioned blend of commercially pure benzole and commercial xylole, or by separating the toluole fraction during distillation and running xylole to the benzole in predetermined amounts ; the product would then approximate to 80 per cent. benzene, 5 per cent. toluene, and 15 per cent. xylenes.[2] According to Kraemer

[1] *British Standards Institution, B.S.* 83, 1922.
[2] Downs, *Chem. and Ind.*, 1932, 51, 28.

and Spilker the following artificial mixtures have the boiling range required for 90's benzole :—

1. 82 per cent. benzene and 18 per cent. toluene.
2. 92·2 per cent. benzene and 7·8 per cent. xylene.
3. 90·0 per cent. benzene, 5·0 per cent. toluene and 5·0 per cent. xylene.
4. 82·0 per cent. benzene, 15·0 per cent. toluene and 3·0 per cent. xylene.

The last named, alone, has the approximate composition of an average commercial 90's benzole.

The solvent properties of a 90's benzole are only slightly affected by such variations in composition. Straight-run benzole is largely produced by manufacturers who do not market special solvents. Other grades of benzole, which are specifically known as non-corrosive commercially pure benzole, are produced specially for lithographic work and in processes where staining of metallic surfaces must be avoided.

The lower grades of benzole may be used for the denaturing of alcohol. Commercial toluole is used as a raw material for organic chemical synthesis ; as a lacquer diluent, as a resin solvent (in place of true nitro-cellulose solvents) ; and for a variety of purposes in the paint, varnish and rubber industries. A non-corrosive grade may be used instead of non-corrosive benzole. The xyloles, of which the pure, the 3° and the 5° are the most important, are used in like manner as general solvents in common with the solvent naphthas, but in particular as solvents for phthalic anhydride resins to produce low viscosity enamels with good flowing properties. When odour and colour are not objectionable, as, for example, in the production of bituminous paints and materials for road surfacing, the crude unrectified solvent naphthas may be employed. Heavy naphthas are used as slow drying solvents in paints and varnishes and for the manufacture of polishes and in linoleum production.

The average compositions of refined solvent naphtha and of heavy naphtha (hiflash) are given below [1] :—

Refined Solvent Naphtha

Constituent.	Per cent. by weight.
Benzene	nil to 1
Toluene	5
Xylenes	80
Ethyl-, propyl-, methyl-, ethyl-benzenes	1 to 3
Trimethyl benzenes	5
Tetramethyl benzenes	5
Naphthalene	1 to 3

Heavy Naphtha (hiflash)

Constituent.	Per cent. by weight.
Ethyl benzenes, xylenes, cumene, propyl benzene, and ethyl toluene	10
Trimethyl benzenes (pseudo cumene predominating)	45
Tetramethyl benzenes (isodurene predominating)	40
Naphthalene	5

[1] Downs, *loc. cit.*

Acid washing of solvent naphtha removes indene (b.p. 182·2° to 182·4°) [1] and coumarone (b.p. 175°) the resins so produced being refined and marketed under the general name of "coumarone" resins (p. 286). The unrectified heavy solvent naphthas contain these bodies also. They approximate in percentage composition by weight to: coumarone, indene, styrene, etc., 40 per cent.; high-boiling naphtha constituents, 40 per cent.; and methyl naphthalenes and naphthalene, 20 per cent. The heavier fractions of the light oil are also used for autogenous welding and for incandescent lighting (Denayouze and Fernholtz's benzole lamp). Solvents for the rubber industry are discussed by Twiss,[2] and Downs [3] surveys the production of solvents in America by the gas industry.

The most important use of benzole to-day is as a motor fuel. Motor benzole is obtained in large quantities by the refining of benzole scrubbed mainly from coke-oven gas and, to a minor extent, from the stripping of town's gas and the distillation of coke-oven and gasworks tars. It is estimated that the production of refined benzole, including benzole for industrial purposes, is approximately 61 million gallons per year. Potential production is considerably higher, since a relatively large amount could be recovered by gas stripping. Estimated production in other countries is as follows:—

	mil. gals.
Germany	135
U.S.A.	118
France	19
Belgium	13
Holland	8
Poland	6·5
Czechoslovakia	5

An average of two gals. per ton of coal carbonized is obtained from by-product coke-ovens in Great Britain. Benzole and benzole-containing motor fuels possess better anti-knock properties, a higher available heat value per unit volume (the higher sp. gr. compensating for its low calorific value), and give a greater mileage per gallon of fuel consumed. Motor benzole is usually sold in admixture with petrol or with the addition of a small proportion of a low-boiling liquid such as ether in order to give ease of starting the engine (the initial distillation point of motor benzole is about 80° compared with 40° for petrol). The results of distillation tests cannot, however, be correlated correctly with the volatility of a benzole and no entirely satisfactory test of volatility has yet been devised.

[1] Spilker and Dombrowski, *Ber.*, 1909, **42**, 572.
[2] *Trans. Inst. Rubber Ind.*, 1926, **2**, 381.
[3] *Chem. and Ind.*, 1932, **51**, 28.

Specifications of quality of a commercial light coal-tar product vary according to the purpose to which it is to be applied. The conditions relate to the boiling range, the sp. gr. at 15° or 15·5°, the behaviour towards sulphuric acid and bromine, the contents of paraffins, thiophen, carbon disulphide and gum-forming substances, as well as to colour and odour, the latter especially in the case of the higher boiling products. According to Kraemer and Spilker the following are the usual commercial products, with their approximate boiling ranges :—

Works designation.	Commercial product.	Boiling range.	Specific gravity: 15°/15°.
Commercial benzole I.	90's benzole	To 100°, 90 per cent. to 120°, 100 ,,	0·880 to 0·883
,, ,, II.	50's benzole	To 100°, 50 ,, to 120°, 90 ,,	0·875 ,, 0·877
,, ,, III.	0's benzole	To 100°, 0 ,, to 120°, 90 ,,	0·870 ,, 0·872
,, ,, IV.	Crude xylole	To 130°, 30 ,, to 145·5°, 90 ,,	...
,, ,, V.	Solvent benzole I.	To 130°, 0 ,, to 160°, 90 ,,	0·870 ,, 0·880
,, ,, VI.	Solvent benzole II.	To 145°, 0 ,, to 175°, 90 ,,	0·880 ,, 0·910
Commercial heavy benzole	Heavy benzole	To 160°, 0 ,, to 195°, 90 ,,	0·920 ,, 0·945
Pure benzene	80°/81° benzole	95 per cent. within 0·8°	0·883 ,, 0·885
Thiophen-free benzene	...	95 per cent. within 0·8°	0·883 ,, 0·884
Toluene	Pure toluene	95 per cent. within 0·8°	0·870 ,, 0·871
Xylene	Pure xylene.	To 136°, 0 per cent. to 140°, 90 ,,	0·867 ,, 0·869
Cumene	...	To 163°, 0 ,, to 172°, 90 ,,	0·886 ,, 0·890
Pseudocumene	...	To 167°, 0 ,, to 170°, 90 ,,	0·888 ,, 0·890

Specifications of the National Benzole Association,[1] and the chief characteristics of German [2] and American [3] light coal-tar products are summarized in the tables which follow.

[1] *Standard Specifications for Benzole and Allied Products*, 1938, The National Benzole Association, London, 1938.

[2] Berl-Lunge, *Chemisch-technische Untersuchungsmethoden*, Berlin, 8th edn., **4**, 275.

[3] Downs, *Chem. and Ind.*, 1932, **51**, 28; Manufacturing Specification for Coke-Oven Light Oil Distillates, The Barrett Company, 1st May 1936.

Typical Light Coal-tar Products, Benzol-Verband, Bochum

Grade name.	Colour.	Specific gravity (approximate).	Distillation range.	Reaction to sulphuric acid (maximum).	Bromine value (maximum).	Remarks.
Commercial 90's benzole .	Water white	0·880	To 100°, at least 90 per cent. and not more than 93 per cent. of distillate.	1·5	0·8	...
Benzole for colour manufacturers	"	0·880	To 100°, at least 90 per cent. and not more than 93 per cent. of distillate.	0·5	0·4	...
Pure benzole . .	"	0·882	90 per cent. within 0·6°. 95 per cent. within 0·8°.	0·3	0·5	No guarantee of the crystallizing point.
Commercial toluole .	"	0·870	First drop not below 100°. To 120°, at least 90 per cent. of distillate.	0·5	0·8	...
Pure toluene . .	"	0·870	90 per cent. within 0·6°. 95 per cent. within 0·8°.	0·3	0·8	...
Commercial xylole .	"	0·860	First drop not below 120°. To 145°, at least 90 per cent. of distillate.	3·0	...	Stable to light.
Pure xylene . . .	"	0·860 to 0·868	90 per cent. within 3·6°. 95 per cent. within 4·5°.	2·0	2·5	...
Solvent naphtha I. .	Water white to light yellow.	0·870	First drop not below 120°. To 160°, at least 90 per cent. of distillate.	3·0	...	Stable to light. faint odour.
Solvent naphtha II. .	"	0·870	First drop not below 135°. To 180°, at least 90 per cent. of distillate.	Separates brownish-yellow resinous masses on standing.	...	Not completely stable to light, odour of tar oils.
Forerunnings . .	...	...	To 79°, at least 60 per cent. of distillate.	...	...	...
Heavy benzole . .	...	...	First drop not below 160°. To 200°, at least 90 per cent. of distillate.	...	...	Not washed with concentrated sulphuric acid ; slight contamination with phenols and bases permissible.

Grade name.	Colour.*	Specific gravity, 15·5° C.	Distillation.			
			First drop.	Per cent. at fixed temperature.	Dry point.	Range.
1. Nitration benzole	Water white	0·8820 to 0·8860	...	Includes 80·2° C.	...	1° C.
2. Non-corrosive commercially pure benzole	,,	0·875 ,, 0·886	...	,, 80·2° C.	...	2° C.
3. Commercially pure benzole	,,	0·875 ,, 0·886	...	,, 80·2° C.	...	2° C.
4. Non-corrosive 90 per cent. benzole	,,	0·870 ,, 0·882	78·2° C.+	90 to 95 per cent. at 100° C.	120° C.−	42° C.
5. Commercial 90 per cent. benzole	,,	0·870 ,, 0·882	76·2° C.+	90 to 95 per cent. at 100° C.	120° C.−	44° C.
6. Motor benzole	,,	...	176° to 180° F. 80° to 82° C.	75 per cent.+ at 100° C.	284° F. 140° C.	±60° C.
7. Motor benzole	,,	0·860 ,, 0·880	168° to 180° F. 76° to 82° C.	60 per cent. at 100° C. 90 ,, ,, 120° C.	338° F. 170° C.	±94° C.
8. Nitration toluole	,,	0·869 ,, 0·873	...	Includes 110·4° C.	...	1° C.
9. Non-corrosive commercially pure toluole	,,	0·864 ,, 0·874	...	,, 110·4° C.	...	2° C.
10. Commercially pure toluole	,,	0·864 ,, 0·874	...	,, 110·4° C.	...	2° C.
11. Commercial toluole	,,	0·860 ,, 0·870	±98° C.	90 per cent. at 120° C.	±132° C.	±34° C.
12. Special commercial xylole	,,	0·860 ,, 0·875	±122° C.	5 per cent.− at 130° C.	150° C.−	±28° C.
13. 3° xylole	,,	0·865 ,, 0·870	137·2° C.	...	140·5° C.	3° C.
14. 5° xylole	,,	0·860 ,, 0·870	137° C.+	...	142° C.	5° C.
15. 10° xylole	,,	0·860 ,, 0·870	135·0° C.	...	145° C.	10° C.
16. Nitration *meta*-xylene	,,	0·865 ,, 0·870	138·3° C.	Includes 139·5° C.	139·7° C.	1·5° C.
17. Solvent naphtha	,,	0·860 ,, 0·875	±125° C.	5 per cent.− at 130° C. 90 to 95 per cent. at 160° C.	180° C.	±55° C.
18. Special washed solvent naphtha	,,	0·860 ,, 0·875	±125° C.	5 per cent.− at 130° C. 90 to 95 per cent. at 160° C.	180° C.−	±55° C.
19. Special solvent naphtha	,,	0·820 ,, 0·850	±140° C.	...	±185° C.	45° C.
20. Crude light solvent naphtha	Light amber to dark red	0·860 ,, 0·875	±125° C.	10 per cent.− at 130° C. 90 per cent.+ at 160° C.	±200° C.	±75° C.
21. Straw colour solvent naphtha	Light straw colour	0·865 ,, 0·895	±125·0° C.	...	±165° C.	±40° C.
22. Cumene	Water white	0·860 ,, 0·880	165·5° C.	50 per cent. from 160° to 171° C.	175·5° C.	±10° C.
23. Low-boiling hiflash naphtha	,,	0·860 ,, 0·890	160·0° C.	...	185° C.	25° C.
24. Hiflash naphtha	,,	0·860 ,, 0·890	150·0° C.	90 per cent. at ±180° C.	200° C.	50° C.
25. High-boiling hiflash naphtha	,,	0·860 ,, 0·890	175·0° C.	...	200° C.	25° C.
26. Heavy solvent naphtha	Amber	0·930 ,, 0·980	±160·0° C.	...	200° C.	±65° C.
27. Heavy solvent naphtha	Amber to red	0·870 ,, 0·890	±150·0° C.	10 per cent.− at 160° C. 90 ,, + ,, 200° C.	215° C.	±65° C.
28. Heavy solvent naphtha	Light amber to dark red	0·925 ,, 0·950	±150·0° C.	10 ,, − ,, 160° C. 70 ,, ,, 200° C. 95 ,, + ,, 260° C.	285° C.	±130° C.
29. Heavy solvent naphtha	Light amber to dark red	0·940 ,, 0·986	±155·0° C.	5 ,, − ,, 160° C. 90 ,, + ,, 200° C.	285° C.	±130° C.
30. Crude heavy solvent naphtha	Light amber to dark red	0·930 ,, 0·986	+115·0° C.	5 ,, − ,, 120° C. 90 ,, + ,, 200° C.	220° C.	±105° C.

* Water-white products are defined as not darker than a

† Acid wash test standards refer to standards of the Barrett

‡ Test may show "peacock" discoloration of copper, but

Flash point. (A.S.T.M. closed cup.)	Acid wash test not darker than.†	Acidity.	Solidifying point.	Sulphur content, as H_2S or SO_2.	Copper dish test.‡
10° to 20° F.	No. 2	None	4·75° C.+	No H_2S. No SO_2	Meets
10° ,, 20° F.	No. 3	None	±41° F. ± 5° C.	,, ,,	,,
10° ,, 20° F.	No. 4	None	±41° F. ± 5° C.	No test	No test
10° ,, 20° F.	No. 6	None	±36° F. ± 2·5° C.	No H_2S. No SO_2	Meets
10° ,, 20° F.	,,	,,	±36° F. ± 2·5 C.	No test	No test
10° ,, 20° F.	,,	None or slightly alkaline	±36° F. ± 2·5° C.	0·40 per cent. —total sulphur	See note 2
10° ,, 20° F.	No. 12	None or slightly alkaline	±36° F. ±2·5° C.	0·50 per cent.—total sulphur	See note 2
±55° F.	No. 2	None	...	No H_2S. No SO_2	Meets
±55° F.	No. 4	,,	...	,, ,,	,,
±55° F.	,,	,,	...	No test	No test
±40° F.	No. 6	,,	...	,,	,,
75° C.+	,,	,,	...	No H_2S. No SO_2	Meets
75° to 80° F.	,,	,,	...	,, ,,	,,
75° ,, 80° F.	,,	,,	...	,, ,,	,,
75° ,, 80° F.	,,	,,	...	,, ,,	,,
75° ,, 80° F.	,,	,,	...	,, ,,	,,
75° F+	No. 12	,,	...	No test	No test
75° F.+	No. 6	,,	...	,,	,,
100° F.+	,,	,,	...	,,	,,
75° F.+	No test	,,	...	,,	,,
75° F.+	,,	,,	...	,,	,,
110° F.+	No. 10	,,	...	No H_2S. No SO_2	,,
100° F.+	No. 9	,,	...	,,	,,
100° F.+	,,	,,	...	,,	,,
100° F.+	,,	,,	...	,,	,,
100° F.+	No test	No test	No $C_{10}H_8$ crystals at −20° C.	No test	,,
100° F.+	,,	,,	,,	,,	,,
100° F.+	,,	,,	,,	,,	,,
100° F.+	,,	,,	,,	,,	,,
±40° F.	,,	,,	...	,,	,,

water solution of potassium dichromate containing 0·0030 g. per 1000 ml. of water.
Company (U.S.A.). (*Cf.* p. 278.)
copper shall not show grey or black discoloration or deposit.

Coke-Oven Light

Grade name.	Odour; colour (not darker than *x* g. of potassium dichromate in 1000 ml. of water).	Specific gravity, 15·5°.	Distillation range.	Sulphur compounds.
1. Nitration benzole	No foreign odour; 0·0030	0·8820 to 0·8860	From start to dry within 1°, and including 80·2°	Free from H_2S and SO_2
2. Industrial pure benzole	,, ,,	0·875 to 0·886	From start to dry within 2°, and including 80·2°	,,
3. Industrial 90 per cent. benzole	,, ,,	,,	First drop not below 78·2°. 90 to 95 per cent. at 100°; dry point not above 120°	,,
4. Nitration toluol .	,, ,,	0·8690 to 0·8730	From start to dry within 1°, and including 110·4°	,,
5. Industrial pure toluol	,, ,,	0·864 to 0·874	From start to dry within 2°, and including 110·4°	,,
6. 3° xylol . . .	,, ,,	0·865 to 0·870	From start to dry within 3°; first drop not below 137·2°; dry point not above 140·5°	,,
7. 5° xylol . . .	,, ,,	0·860 to 0·870	From start to dry within 5° and including 139·5° (b.p. *m*-xylene); first drop not below 137°; dry point not above 143°	,,
8. 10° xylol . . .	,, ,,	,,	From start to dry within 10°; first drop not below 135°; dry point not above 145°	,,
9. Industrial xylol .	,, ,,	,,	First drop not above 135°. Not more than 5 per cent. by volume at 130°; 90 to 95 per cent. at 145°; dry point not above 155°	,,
10. Solvent naphtha .	,, ,,	0·855 to 0·870	,, ,,	,,
11. Standard motor benzole	,, ,,	Not below 0·870	First drop between 76° and 82°; 60 per cent. by volume at 100°; 90 per cent. by volume at 120°; dry point not above 170°	Total sulphur not greater than 0·40 per cent. by weight
12. Crude light solvent naphtha	No foreign odour; light amber colour	0·860 to 0·885	First drop not above 135°. Not more than 5 per cent. by volume at 130°; 90 to 95 per cent. at 160°; dry point not above 180°	No test
13. Heavy solvent naphtha	No foreign odour; light amber to dark red in colour	0·885 to 0·970	Not more than 5 per cent. by volume at 150°; 5 per cent. by volume at 165°; 90 per cent. by volume at 200°; dry point not above 220°	,,

Oil Distillates

Solidifying point.	Acid wash. Barrett colorimetric scale number.	Acidity.	Copper corrosion test.	Remarks.
Not less than 4·85° (dry basis)	Not darker than No. 2	No evidence of acidity	To pass	..
No test	Not darker than No. 3	,,	,,	...
,,	Not darker than No. 6	,,	,,	..
,,	Not darker than No. 2	,,	,,	...
,,	Not darker than No. 4	,,	,,	...
,,	Not darker than No. 6	,,	,,	Paraffin content not more than 4·0 per cent. by volume. Desirable that it be not more than 0·5 per cent.
,,	,,	,,	,,	...
				...
,,	Not darker than No. 10	,,	,,	Paraffin content not more than 10·0 per cent. by volume. Desirable that it be not more than 3·0 per cent.
,,	,,	,,	No test	...
,,	Not darker than No. 12	,,	May show iridescent or peacock discoloration, but not grey or black, or deposit	...
,,	No test	..	No test	...
,,	,,	,,	,,	Tar acid content not more than 3 per cent. by volume. Dry salts (naphthalene) not more than 8 per cent. by weight

The composition of commercial light coal-tar products is approximately as follows (F. Frank) [1] :—

	90's benzole.	50's benzole.	0's benzole.	Solvent naphtha to 160°.	Solvent naphtha to 175°.	Heavy benzole.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Benzene	84	43	15	...	...	...
Toluene	13	46	75	5	...	...
Xylene	3	11	10	70	35	5
Cumene	...	...	...	25	60	80
Neutral naphthalene oil	...	...	...	...	5	15

Coumarone and indene are not accounted for in this table; the latter is contained in the heavy benzole up to 40 per cent., and also to about 6 per cent. in the slightly washed naphtha, boiling up to 175°. Further, the proportion of paraffins, carbon disulphide, thiophen, etc., is not included.

As an average of many years' observations, Kraemar and Spilker [2] give the composition of commercial benzoles used in colour works as follows :—

	90's benzole.	50's benzole.	0's benzole.	Remarks.
	Per cent.	Per cent.	Per cent.	The water in 90's benzole is usually found in summer only, and then only shortly after its manufacture.
Water	0·06	...	...	
Paraffins	0·10	0·25	0·50	
Carbon disulphide	0·69	0·39	...	
Compounds absorbing bromine	1·20	1·23	0·82	
Thiophen (in above)	(0·26 per cent.)		...	
Benzene	80·92	45·37	13·54	
Toluene	14·85	40·32	73·42	
Xylene	2·18	12·44	11·69	

The boiling ranges of the commercial products given in the above tables, at the normal pressure of 760 mm. are as follows :—

Commercial benzole I. (90's benzole).	Commercial benzole II. (50's benzole).	Commercial benzole III (0's benzole).	Commercial benzole IV. (crude xylene).
Per cent.	Per cent.	Per cent.	Per cent.
81·0° to 85° = 48·0	78·0° to 90° = 3·0	101° to 105° = 11·0	125° to 130° = 30·0
„ 90° = 78·0	„ 95° = 31·0	„ 110° = 49·0	„ 135° = 60·0
„ 95° = 87·5	„ 100° = 52·0	„ 115° = 79·0	„ 140° = 87·0
„ 100° = 91·5	„ 105° = 67·0	„ 119·5° = 90·0	„ 141·5° = 90·0
...	„ 110° = 77·0	„ 120° = 91·0	...
...	„ 115° = 84·0	„ 125° = 95·0	...
...	„ 120° = 90·0	...	...

[1] *Chem. Ind.*, 1901, **24**, 239.

[2] Muspratt, *Handbuch der technischen Chemie*, 4th edn., **8**, pp. 33 *et seq.*

Commercial benzole V. (solvent naphtha I.).	Commercial benzole VI. (solvent naphtha II.).	Commercial heavy benzole.	Pure benzene (80/81° benzole).
Per cent.	Per cent.	Per cent.	Per cent.
135° to 140° = 20·0	147° to 150° = 5·0	160° to 165° = 15·0	79·5° to 79·6° = 2·0
,, 145° = 50·0	,, 155° = 25·0	,, 170° = 45·0	,, 79·8° = 6·0
,, 150° = 75·0	,, 160° = 50·0	,, 175° = 70·0	,, 80·0° = 10·0
,, 155° = 85·0	,, 165° = 72·0	,, 180° = 82·0	,, 80·1° = 65·0
,, 159° = 90·0	,, 170° = 84·0	,, 187° = 90·0	,, 80·2° = 94·0
,, 160° = 91·0	,, 173° = 90·0	,, 190° = 91·0	...
...	,, 175° = 91·0	...	...

Toluene.	Cumene.	Pseudocumene.
Per cent.	Per cent.	Per cent.
110·2° to 110·3° = 15·0	165° to 166° = 7·0	166° to 167° = 30·0
,, 110·4° = 35·0	,, 168° = 37·0	,, 168° = 90·0
,, 110·5° = 70·0	,, 170° = 70·0	,, 168·5° = 95·0
,, 110·6° = 90·0	,, 172° = 90·0	...
,, 110·7° = 95·0	...	...

The requirements of the British Standard Specification for Motor Benzole [1] are those given for Motor Benzole in the above table of Light Coal-Tar Products of the National Benzole Association.

Pure benzene is a colourless liquid with a b.p. of 79·6° [2] to 80·2° [3], and with a sp. gr. varying with temperature as indicated below :—

$t°$.	Specific gravity.*	Specific gravity.†	$t°$.	Specific gravity.*	Specific gravity.†
0·0	...	...	31	...	0·8659
10·0	0·8893	0·8878	40	0·8571	0·8559
15·5	0·8834	0·8824	50	0·8464	0·8456
20·0	0·8785	0·8776	60	0·8356	0·8358
25·0	0·8731	...	70	0·8252	0·8237
30·0	0·8678	...	...	...	...

* Spielmann and co-workers, *D.E.S. Laboratory, Ministry of Munitions.*
† Parker and Thompson, *J. Chem. Soc.*, 1922, **121**, 1341.

The crystallizing point is 5·5° and the heat of combustion at constant volume [4] is 10,014 cal. per g. On mixing water with the corresponding quantities of benzene no volume change occurs.

[1] *British Standards Institution, B.S.* 135, 1939 (price 3s. 6d.).
[2] *Inter. Crit. Tables*, vol. i., p. 176.
[3] Giffard and Lowry, *Proc. Roy. Soc.*, 1923, A. **104**, 430.
[4] Richards and Shipley, *J. Amer. Chem. Soc.*, 1914, **36**, 1835.

The solubility of water in benzene is as follows [1] :—

$t°$.	Water. Per cent.	$t°$.	Water. Per cent.
5·4	0·034	50·0	0·156
15·0	0·054	57·5	0·185
25·0	0·073	65·0	0·238
37·5	0·115	69·5	0·265

Pure toluene is a colourless liquid with a b.p. of from 110·5° [2] to 110·8°,[3] and with a sp. gr. of 0·882 at 0° and 0·872 at 15°. The crystallizing point is −95·1°, and the heat of combustion is 10,158 cal. per g.[4]

The properties of the three *xylenes* are given in the following table :—

	Specific gravity.*		Boiling point.† °C.	Crystallizing point. °C.
	at 15°.	at 20°.		
o-xylene	0·885	0·879	144	−28·0
m-xylene	0·869	0·865	139	−54·8
p-xylene	0·866	0·861	138	13·0

* Auwers, *Annalen*, 1919, **419**, 92.
† Richards and Jesse, jun., *J. Amer. Chem. Soc.*, 1910, **32**, 268.

(*b*) Colour

The colour of a product is a rough indication of its purity. Colour is objectionable in a solvent, but has little connection with the performance value of a motor benzole. Colour should be measured comparatively with a standard solution of potassium dichromate and cobalt sulphate in water, using a Lovibond or other standard tintometer. The term *water white*, in common use in America, implies a product which is not darker than a solution of 0·0030 g. of potassium dichromate in 1 litre of water. In the case of unrectified products, when colour is described, the limits are from colourless through pale yellow or light amber to dark brown or dark red. Absence of colour is no criterion of freedom from gum, certain gum-forming constituents possessing very little colour.

[1] Spielmann, *Constituents of Coal Tar*, London, 1924, p. 39.
[2] *Inter. Crit. Tables*, vol. i., p. 176.
[3] Spielmann and Wheeler, *Tables of Chemical and Physical Constants of Light Naphtha* H.M. Stationery Office, 1918.
[4] Richards and Davis, *J. Amer. Chem. Soc.*, 1917, **39**, 341.

The Standard Method, devised for use in the specifications of the National Benzole Association and the British Standards Institution, stipulates that the sample be first filtered through filter paper (*e.g.* Whatman No. 5), the first 10 ml. of filtrate being rejected. 50 ml. of the filtered sample is then compared with 50 ml. of the standard colour solution prescribed in the specification, the comparison being made in matched British Standard Nessler cylinders (50 ml. size) held three inches above the surface of an opaque opal glass sheet reflecting diffused daylight.

(*c*) Specific Gravity and Density

Standard Methods recognizes both the hydrometer and the bottle methods, the latter being generally preferred and indeed necessary when particular accuracy is required. A bottle provided with a cap to prevent loss of volatile constituents should be used.

The Barrett Company of America specify the use of a standard Westphal balance. A standard hydrometer of suitable range is frequently employed or a pyknometer may be used when great accuracy is required. The sp. gr. of a benzole is no reliable criterion as to its nature since it is markedly influenced by the character of the impurities present. With a sulphuric acid-refined benzole, however, it indicates whether the product consists essentially of aromatic hydrocarbons, or contains appreciable quantities of paraffins, unsaturated hydrocarbons and carbon disulphide. If amongst the latter the specifically heavier carbon disulphide predominates, the sp. gr. will be higher than when the lighter hydrocarbons form the major portion of the impurities, and, again, the sp. gr. may be approximately normal if both classes of compounds are present together in such proportion that their effects are neutralized. With solvents of wide boiling range the sp. gr. may serve to indicate a natural mixture or a blend ; with products which are not acid-refined the sp. gr. must be considered in conjunction with the results of distillation and other tests.

(*d*) Water

Water may be determined as for light oil (p. 178), but no Standard Method is prescribed, as neither the National Benzole Association specifications nor those of the British Standards Institution permit the presence of undissolved water in refined lower boiling fractions while, as has been seen, the potential amount of dissolved water is extremely limited. Water is a particularly objectionable constituent and the utmost effort compatible with commercially economic manufacturing technique is made to ensure its absence.

(e) Distillation or the Determination of the Boiling Range

The distillation range of a product is an important indication of its general composition and is generally closely specified either according to the volume distilling over a certain defined range or ranges of temperature or by the first drop and dry points and the percentages over at intermediate stages. The conditions of testing, however, have a very marked effect on the results obtained. Thus a considerable divergence may be expected between results obtained by the " retort " method and the " flask " method, and the results obtained with the flask provided with a particular type of column and the flask without a column. A standard distillation test will give a general indication of the volatility of a benzole at room temperature and show the presence of too high a proportion of volatile constituents or heavy ends. Strict observance of the specified conditions of a test is essential and with the purer hydrocarbons account must be taken of the barometric pressure.

In this country it was the common practice to base commercial contracts upon Allen's [1] Retort Test, but with the institution and adoption of standard methods the Retort Test has been superseded, so far as refined products are concerned, by the flask distillation test described later. The flask distillation test is standard practice in the United States. Allen's Retort Test is described by its author as follows :—

100 ml. of the sample (say, a 90's benzole) is measured in an accurately graduated cylinder and poured thence into a tubulated retort of such a size as to be capable of containing 200 ml. when placed in the ordinary position of distillation. The retort should be rinsed previously with some of the sample to be tested. A delicate thermometer is fitted in the tubulure of the retort by a cork, so that it may be vertical and the lower end of the bulb be ⅜ in. distance from the bottom of the retort. The thermometer should be 14 in. long and its bulb sufficiently small to ensure complete immersion in the liquid. The first division on the stem should be 70°, which point should be well out of the tubulure of the retort and the graduations should be continued in tenths of a degree up to 130°. The neck of the retort is inserted into the inner tube of a Liebig condenser and pushed down as far as it will go. The condenser should be from 15 to 18 in. in length, and well supplied with cold water. No cork or other connection is necessary between the retort, neck and the condenser tube. Before use, the tube of the condenser should be rinsed or sprayed with a little of the sample and allowed to drain. The graduated cylinder employed for measuring out the sample is next placed under the further end of the condenser tube in such a manner as to catch all the distillate whilst allowing it to drop freely. The retort is then heated by the naked flame of the Bunsen burner provided with an air-regulator which works automatically with the movements of the tap and surrounded with a screen to exclude draughts. The flame should be small, about the size and shape of a filbert, and when the distillation of the benzole commences, it must be so regulated that the condensed liquid shall fall rapidly in distinct drops, but not in a trickle or continuous stream. When distillation begins the rise of the thermometer is carefully

[1] *Commercial Organic Analysis*, London, 4th edn., 1914, Vol. III., p. 231.

watched. The moment it reaches 85° (or as much below this temperature as will allow the "after-rise" to bring the thermometer to this temperature) the flame is extinguished. Four or five minutes are allowed for the liquid in the condenser to drain into the measuring cylinder and then the volume of the distillate is read off and recorded. The burner is then relighted and the distillation continued till the thermometer rises to 100°, when the gas is turned off as before, and the volume of the distillate read off after allowing time for draining. The residual liquid in the retort is allowed to cool and is then poured to the last drop into the measuring cylinder. Any deficiency from the 100 ml. originally taken is regarded as "loss by evaporation or other natural causes," and is to be added to the measure of the distillate collected at each temperature. The corrected volumes are reported as the "strength" of the benzole at the respective temperatures. It is very desirable to observe the barometric pressure before making an experiment. A difference of 1 in. in the height of the barometer makes a difference of 1° in the boiling point and hence, if the barometer registers 29·5 in. instead of 30 in., the gas should be extinguished so that the thermometer may show a temperature of 99·5° instead of 100°.

A more reliable method than the above for the assay of commercial benzoles, and which is in general use in Germany, is the result of a proposal due to Lunge [1] for the attainment of uniform methods of analysis.

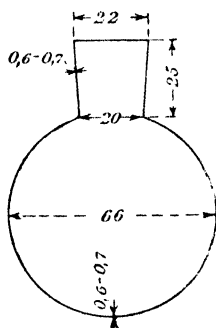



FIG. 36.

It is based upon the employment of an apparatus proposed by Bannow in 1886, and makes use of the results obtained by Lenders [2] on the influence of the height of the barometer upon the boiling point of benzene hydrocarbons. The apparatus for carrying out the distillation, as described by Kraemer and Spilker,[3] is shown in Figs. 36 and 37. A spherical vessel (Fig. 36) made of strong copper 0·6 to 0·7 mm. thick, which is slightly flattened at the bottom, is used for the distillation. It has a neck 25 mm. long, the diameter of which is 22 mm. at the top and 20 mm. at the bottom, for the reception of the glass prolongation, which is 150 mm. long and 14 mm. wide. In the middle of the glass portion is a bulb of 30 mm. diameter, above

[1] *Chem. Ind.*, 1884, **7**, 50.
[2] *Ibid.*, 1889, **12**, 169.
[3] Muspratt, *Handbuch der technischen Chemie*, 4th edn., **8**, 35.

which, at a distance of 10 mm., a side-tube of 8 mm. diameter is sealed almost at right angles. The glass column and the spherical vessel are connected by means of a good cork stopper. A Bunsen burner of about 7 mm. diameter or a benzene spirit lamp is used for heating. The burner is placed in a tinplate cylinder provided with a door, and also with four round holes 10 mm. above the bottom, and four more 10 mm. below the top, for ventillation (Fig. 37). This small heater is covered at the top with a sheet of asbestos having a round hole of 50 mm. diameter in which the spherical retort is placed. The inner tube of the glass Liebig condenser has a length of 800 mm., and is inclined with the outlet 100 mm. below the level of the inlet. The thermometer is made of thin glass, and is graduated in $\frac{1}{10}$ths of a degree for pure benzene, and in $\frac{1}{5}$ths of a degree for commercial

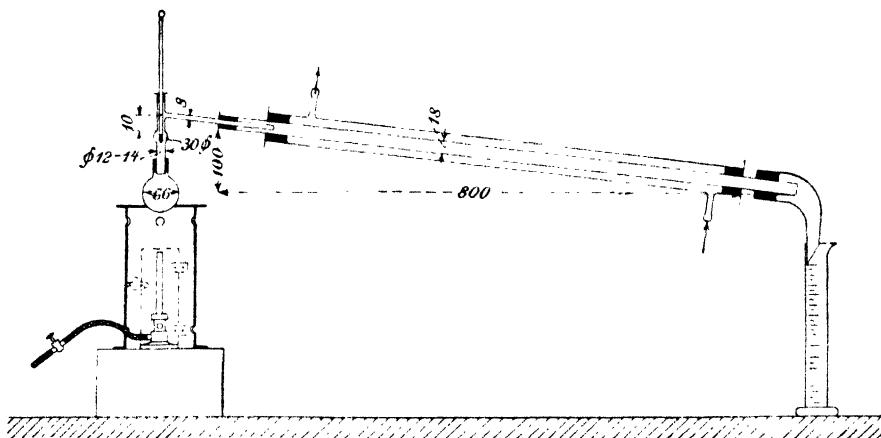



FIG. 37.

products; it should be about one-half the diameter of the neck, and must be so fixed that its bulb is exactly in the middle of the widened part; it should be compared from time to time with a standard thermometer. The distillate leaves the condenser through a bent adapter and runs down the sides of a 100 ml. graduated cylinder.

To carry out the evaluation, 100 ml. of the liquid is put into the flask, and the distillation is conducted so that 5 ml. distils over per minute, *i.e.*, two drops per second; it is complete when 95 ml. has distilled over. In order to correct any cause of error due to different barometer readings, the method of Bannow can be employed, in which the thermometer reading is checked by distilling 100 ml. of water in the same vessel, and observing the thermometer reading at the boiling point of the water, when 60 ml. of the water have distilled over. It is simpler, however, to utilise Lenders' corrections.[1]

[1] *Chem. Ind.*, 1889, **12**, 169.

The Standard Method, which in principle is applicable to all commercial refined lower boiling products, is carried out in the British Standard distillation apparatus assembly type 1 [1]; a standard thermometer appropriate in range for the particular material being tested is used. Certain items in the assembly as described in the British Standard require to be particularized as compared with the general provisions of the standard (see Fig. 38), and it should be noted that a standard flask of 150 ml. distillation capacity is used with the standard bent end Liebig condenser. A standard 100 ml. Crow receiver is used as the receiver, and no alternative to the Bunsen burner is recognized for heating.

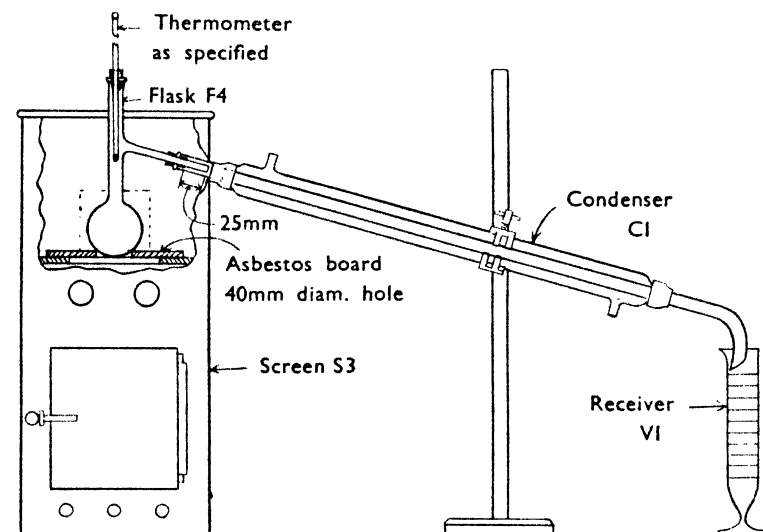



FIG. 38.—Distillation of Refined Lower Boiling Products—Assembled Apparatus.

100 ml. of the sample is distilled, at first slowly so that the mercury column of the thermometer may be fully expanded when the first drop of distillate falls into the receiver. On the other hand, the initial heating period must not be unduly prolonged. A minimum of five minutes and a maximum of ten minutes is allowed from the commencement of heating to the time when the first drop falls into the receiver.

An adequate stream of cooling water must be passed through the condenser; the distillate must collect at a temperature within $\pm$ 5° C. of that at which the sample was measured and when this is impracticable (*e.g.* when testing particularly volatile samples), running point determinations must not be regarded as accurate.

The receiver is placed so that the condensate falls down its side; if the drip-point is to be determined, the receiver is so placed

[1] *British Standards Institution*, *B.S.* 658, 1936.

immediately after the drip-point determination. In this connection it should be noted that *Standard Methods* points out that the temperature at which 5 per cent. of distillate collects is a better guide to the presence of low-boiling constituents than is the drip point; similarly, the 95 per cent. distillate point serves to detect high-boiling constituents more reliably than the dry point, which is unavoidably affected by the superheating of the vapours under the conditions of any practical distillation test. In the circumstances the drip point and dry point are not to be recommended as criteria of lower boiling products.

After the drip point has been reached (and noted if so demanded), the distillation rate is increased to between 4 and 5 ml. per minute and readings of volume and temperature are taken according to the specification or other instructions which are being followed. Temperature corrections are applied to the thermometer readings, in accordance with provisions already described (see p. 134).

The distillate is finally brought to laboratory temperature and measured. The residue in the flask is transferred while hot to a suitable graduated receiver, cooled to laboratory temperature, and measured. Any difference between the combined volumes of the distillate and residue, and the original volume of sample taken for test, is reported as a "distillation loss."

The results of repeat determinations on portions of the same sample, when the tests are carried out with full compliance with the provisions of *Standard Methods*, are stated to be :—

(*a*) $\pm 0.05°$ C. of the average of the several determinations of the difference in temperature, T° C., at which V_1 ml. and V_2 ml. of distillate have collected, provided T be not more than 5; and

(*b*) ± 0.5 ml. of the average of the several determinations of the volume of distillate collected at a specified temperature.

For the assay of commercial benzole, naphthas, solvents, and the like, the Barrett Company of America use a flask method which is comparable to the above Standard Method and applicable, in general, to light oil, pure benzole, toluole and xylole. The dimensions of the flask are given on p. 454.

A standard thermometer is used with a range of from 70° to 120° for nitration and industrial pure benzole and toluole and of from 110° to 160° for pure xyloles, the graduations being at each 0·2°. For industrial 90's benzole and motor benzole and industrial xyloles and naphthas an American Society for Testing Materials High Distillation Thermometer of 0° to 400° range is employed. In the distillation of nitration and industrial pure benzole, and toluoles, a 1 inch hole is provided in the centre of the asbestos support. For other materials boiling substantially below 145° a 1½ inch hole is provided, but for materials having a dry-point above 200°, the hole in the asbestos is increased to 2 inches.

Distillation is continued at a rate of between 5 and 7 ml. per minute (2 drops per second), and the temperature is recorded at the first drop and at every 10 per cent. of distillate until a dry point is reached, except in the case of crude materials when a decomposition rather than a dry point is obtained. When a decomposition point is reached the temperature will cease rising and begin to fall. The highest temperature is noted and the distillation is stopped.

The Retort Test although used widely for the commercial evaluation of benzoles has marked limitations as compared with the flask method, particularly in indicating the presence of forerunnings in the sample under test.

The following data [1] give the results obtained with a number of samples of crude benzole using various distillation methods.

		Retort test.	Standard flask.	Difference between retort and flask.	14-in. Lessing column.	4-ft. Dufton column.	Temperature in standard flask distillation at which amount at 120° (stop point) in retort test had collected.
							°C.
Drip point °C.	1.	87·0	72·5	...	50·0	38·0	...
	2.	86·5	74·0	...	53·0	47·0	...
	3.	90·7	72·5	...	42·0	35·0	...
	4.	91·2	72·5	...	46·0	37·0	...
	5.	85·0	73·5	...	63·0	49·0	...
Per cent. at 75° (running point).	1.	nil	0·2	...	1·1	1·5	...
	2.	,,	0·1	...	0·9	0·9	...
	3.	,,	0·2	...	1·7	1·3	...
	4.	,,	0·1	...	1·2	1·5	...
	5.	,,	0·1	...	0·8	0·5	...
Per cent. at 79° (running point).	1.	,,	1·1	...	3·1	2·8	...
	2.	,,	1·1	...	2·9	2·6	...
	3.	,,	0·8	...	3·3	2·4	...
	4.	,,	0·6	...	2·8	2·5	...
	5.	,,	0·9	...	3·0	1·7	...
Per cent. at 120° (stop point).	1.	69·0	77·5	8·5	76·5	78·5	104·2
	2.	69·5	78·0	8·5	77·5	79·5	102·3
	3.	57·5	69·5	12·0	70·5	71·0	104·7
	4.	56·0	68·0	12·0	67·0	68·5	103·8
	5.	75·5	82·0	6·5	81·5	82·0	104·5
Per cent. residue at 120°.	1.	30·2	21·3	...	18·5	20·5	...
	2.	29·2	21·0	...	17·5	19·5	...
	3.	41·2	29·5	...	24·0	27·8	...
	4.	42·8	31·3	...	27·5	30·5	...
	5.	23·3	17·2	...	14·0	16·8	...
Per cent. distillation loss.	1.	0·8	1·2	...	5·0	1·0	...
	2.	1·3	1·0	...	5·0	1·0	...
	3.	1·3	1·0	...	5·5	1·2	...
	4.	1·2	0·7	...	5·5	1·0	...
	5.	0·7	0·8	...	4·5	1·2	...

[1] Private communication by T. Callan.

Separate 100 ml. portions of the samples were distilled from (1) an 8-oz. retort; (2) a standard flask observing the standard procedure; (3) a flask fitted with a 14-in. Lessing column and a vertical condenser, distillation being at the rate of 5 ml. per minute, except towards the end of the distillation when the speed could not be maintained at a higher rate than 3 to 4 ml. per minute; and (4) a flask fitted with a 4-ft. Dufton column and a vertical condenser, a distillation rate of 5 ml. per minute being maintained except towards the end of the distillation.

Five samples of crude benzole were employed, numbers 2 and 3 being from the same source and 1, 4 and 5 from different sources. The results are tabulated on the preceding page.

		Retort test.		Standard flask.		Difference between retort and flask.		14-in. Lessing column.		Temperature in standard flask distillation at which amount at 120° in retort test had collected.	
		3 per cent.	5 per cent.	3 per cent.	5 per cent.	3 per cent.	5 per cent.	3 per cent.	5 per cent.	3 per cent.	5 per cent.
										° C.	° C.
Drip point °C.	1.	86·5	84·8	69·5	67·0	...	...	45·0	41·0	...	...
	2.	85·3	83·8	72·3	69·0	...	...	46·0	43·0	...	...
	4.	90·0	87·0	70·0	65·3	...	...	42·5	37·0	...	...
	5.	84·6	83·8	73·3	69·0	...	...	52·0	39·0	...	...
Per cent. at 75° (running point).	1.	nil	nil	0·4	1·0	...	...	2·6	4·2	...	...
	2.	,,	,,	0·3	0·6	...	...	2·2	3·3	...	...
	4.	,,	,,	0·2	0·9	...	...	2·7	4·5	...	...
	5.	,,	,,	0·1	0·6	...	...	1·5	4·0	...	...
Per cent. at 79° (running point).	1.	,,	,,	2·5	4·0	...	...	5·8	10·5	...	...
	2.	,,	,,	2·2	3·6	...	...	5·7	8·5	...	...
	4.	,,	,,	1·2	3·8	...	...	5·5	9·5	...	...
	5.	,,	,,	1·5	4·5	...	...	5·2	11·5	...	...
Per cent. at 120° (stop point).	1.	69·2	69·5	77·5	78·0	8·3	8·5	77·5	77·5	104·8	104·7
	2.	69·8	70·0	78·2	78·5	8·4	8·5	78·5	78·5	102·5	102·8
	4.	56·5	57·0	68·5	69·0	12·0	12·0	69·0	69·5	104·7	103·8
	5.	76·0	76·5	82·5	83·5	6·5	7·0	82·5	83·0	105·0	105·0
Per cent. residue at 120°.	1.	29·7	29·7	21·5	21·2	...	...	17·5	17·0	...	...
	2.	28·8	28·8	21·0	20·7	...	...	16·0	16·0	...	...
	4.	42·3	41·8	30·5	30·3	...	...	25·5	25·7	...	...
	5.	23·0	22·5	16·3	15·8	...	...	13·5	12·0	...	...
Per cent. distillation loss.	1.	1·1	0·8	1·0	0·8	...	...	5·0	5·5	...	...
	2.	1·4	1·2	0·8	0·8	...	...	5·5	5·5	...	...
	4.	1·2	1·2	1·0	0·7	...	...	5·5	4·8	...	...
	5.	1·0	1·0	1·2	0·7	...	...	4·0	5·0	...	...

The samples were low in forerunnings. Whereas no indication of the presence of forerunnings is shown by the retort test, the Standard

Flask Method indicates their presence at 75°; at 79°, the amount is about one-third of the total amount given by the Lessing or Dufton columns. The Lessing and Dufton columns will be seen to give parallel and, in many cases, practically identical results throughout the whole of the distillation. The Lessing column, however, retained a considerable amount of distillate, hence showing a high distillation loss.

Distillation of identical samples of crude benzole, to which had been added respectively 3 per cent. and 5 per cent. of synthetic forerunnings consisting of one volume of carbon disulphide, two volumes of petroleum ether (b.p. 40° to 60°) and two volumes of petroleum ether (b.p. 65° to 75°) gave the results shown on the opposite page.

The limitation of the Retort Test as a means of indication of the presence of forerunnings is again shown; the yields at 120°, as given by the Retort Test and the Standard Flask Method, vary from 7 to 12 per cent. The temperature at which the Standard Flask Method gives distillates agreeing with the Retort Test at 120° is approximately 105°. The average difference on a normal 65/120 (retort test) benzole is 10 per cent. greater distillate from the flask than the retort.

(*f*) Crystallizing Point

The British Standard specifications for refined lower-boiling products variously require a test for the determination of crystallizing point. The apparatus is shown in Fig. 201, a standard thermometer being used, the range of which is $-10°$ to $+20°$ C.

If the sample is to be examined on the dry basis, it is dried by shaking for ten minutes with finely powdered plaster of Paris, followed by decanting. Otherwise about 20 g. of the material for test is placed in the inner tube of the crystallizing point apparatus, and a preliminary rapid cooling is carried out to determine the approximate crystallizing point. The tube is then warmed gently until all but the last traces are melted. It is then placed in the jacket of the apparatus and the assembled apparatus placed in a cooling bath 6° to 8° C. below the expected crystallizing point. With continuous but gentle stirring, time and temperature readings are taken at half-minute intervals.

The crystallizing point is normally represented by the first five consecutive readings during which the temperature is constant to within a tenth of a degree. If supercooling takes place the subsequent rise in temperature must not exceed a degree. If after supercooling there is no constant temperature a graph is drawn for time and temperature and the mean line between the first and second and between the fifth and sixth of the six readings, starting with the

maximum temperature after supercooling, is drawn and produced backwards until it intersects the portion of the curve before the supercooling section. The point of intersection is reported as the crystallizing point in this case.

Certain benzoles, such for example as motor benzole, crystallize with no supercooling and the temperature does not remain constant during the crystallization period. The crystallizing point is then taken as the temperature at which the thermometer ceases to be visible.

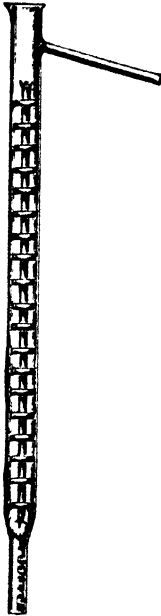
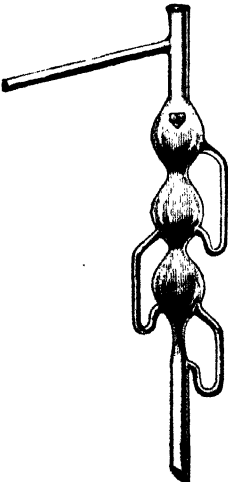
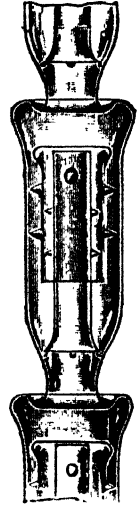
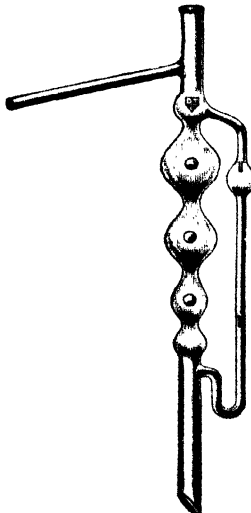
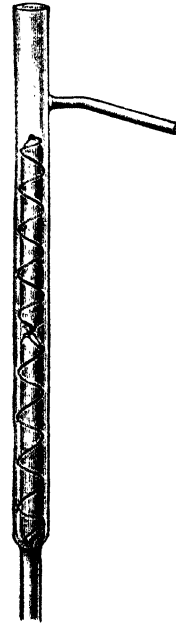
(g) Estimation of Individual Benzene Hydrocarbons

1. **General Methods.**—Standard Methods for the quantitative estimation of benzene hydrocarbons and of impurities such as paraffin hydrocarbons (including naphthenes), and carbon disulphide have now been developed. These methods, which involve fractional distillation, are described later. It is common practice, both in England and Germany, to estimate the benzene, toluene and xylene contained in commercial benzoles by fractional distillation alone, using an efficient column. The boiling points of the constituents lie far apart:—Benzene = 80·2°; Toluene = 110·5°; Xylenes = 138·4° to 144°; Cumenes = 153° to 155°. Several forms of fractionating columns are shown in Fig. 39; they are known respectively as the "Pear," the "Rod and Disc," the "Young and Thomas," [1] the "Le Bel-Henninger," the "Glynsky," the "Dufton" [2] and the "Lessing." [3]

Of these, two may be described. A Dufton column consists of a tube, about 120 cm. in length, and of a cross-section which increases in diameter downwards. A spiral track in a narrow annulus is created within the tube by the insertion of inner tubes round which are wound spirals of wire increasing in pitch from the top section to the bottom section. Thus, a top section may just admit a spiral wire of 0·7 mm. diameter wound round a core of 1·4 mm. diameter, the succeeding section a wire of 1 mm. diameter, a third section 1·2 mm. diameter, and the last 1·4 mm. diameter, wound spirally on similar cores with an increase of pitch from 6 mm. at the top to 12 mm. at the bottom. The condensed liquid returns freely to the flask owing to the graduation of the spiral track, the ascending vapours being caused to pass along the spiral track and to be scrubbed effectively by the descending liquid. The column may be protected from too rapid cooling by wrapping with cotton wool, held in position by asbestos yarn.

[1] Young, *J. Chem. Soc.*, 1899, **75**, 679; *cf.* also *Fractional Distillation*, 1903.

[2] Dufton, *J. Soc. Chem. Ind.*, 1919, **38**, 45 T.

[3] Lessing, *ibid.*, 1921, **40**, 115 T.

Pear.
Rod and Disc.
Young and Thomas.
Le Bel-Henninger.
Glynsky.
Dufton.
Lessing.
Fig. 39.

Gooderham [1] states that the Dufton column is capable of giving good separation of liquid mixtures, but that at temperatures above 100°, even with good lagging, the column is apt to choke. By surrounding the column with a silvered vacuum jacket which has been properly evacuated, however, extremely sharp separations can be obtained up to high temperatures.

The feature of the Lessing column is in the nature of the filling material, namely, Lessing patent contact rings.[2] These consist of metal cylinders of approximately equal height and diameter, having a gap in the circumference and a more or less diametrical partition connected on one side with the cylinder, but not reaching the cylinder at the opposite side. They are disposed indiscriminately in a plain glass or metal tube of the Hempel type. Split rings of this type, in place of the plain cylindrical Raschig rings,[3] are stated to increase considerably the efficiency of condensation. Distillation of a 1 : 1 mixture of benzene and toluene gave a separation of 47 per cent. benzene and 48 per cent. toluene respectively, each fraction distilling within 1° and only 5 per cent. of the total mixture constituted the middle fraction. Comparative experiments with other forms of columns placed these in the following order of efficiency:—Lessing contact rings in a plain tube (4 cm. diameter by 140 cm. high); Young and Thomas dephlegmator, 18 sections (130 cm. high); Young evaporator still-head, 5 sections (75 cm. high); Hempel still-head with glass beads (3 cm. diameter by 35 cm. high); and Glynsky still-head with three bulbs (3 cm. diameter).

The following table gives the results of a single distillation of a mixture of equal weights of pure benzene (b.p. 80·2°) and pure toluene

Temperature range.	Ordinary distillation bulb.	Hempel column.	Rod and disc column (20 discs).	Pear column (13 pears).	Le Bel-Henninger column (3 bulbs).	Young and Thomas column (18 sections).
80·2° to 81·2°	none	20·6	none	none	none	31·5
81·2° „ 83·2°	„		2·0	3·0	0·5	7·3
83·2° „ 107·9°	82·4	39·3	64·7	59·4	68·9	14·4
107·9° „ 110·3°	6·8	6·8	7·4	5·0	9·8	4·0
110·3° „ 110·9°	5·9	8·4	7·5	11·0	6·8	8·1
Residue	4·9	24·9	18·4	21·6	14·0	34·7

(b.p. 110·5°) with different fractionating columns, using 50 g. of the mixture. The distillate was collected in each case in eleven fractions at intervals of about 3°, the residue after the boiling point of toluene

[1] *J. Soc. Chem. Ind.*, 1935, **54**, 297 T.
[2] B.P. 139880, 1919.
[3] B.P. 6288, 1914; *J. Soc. Chem. Ind.*, 1914, **33**, 907.

had been reached forming a twelfth fraction. The same rate of distillation (one drop per second) was maintained throughout, as it was found that this factor has a marked influence on the efficiency of the separation. The distillates at each temperature are given in percentages.

According to Kraemer and Spilker, the rectification test is carried out by general agreement in a copper still of the form and dimensions shown in Fig. 40, 1 kg. of benzole being used, and the vapour passed through a Le Bel-Henninger column 60 cm. long. The thermometer, the position and diameter of the condenser, and the rate of distillation are the same as described on p. 222; the distillate is, however, collected in tared flasks and weighed.

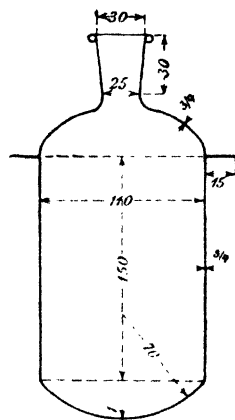



FIG. 40.

The single fractions are generally collected as follows:—

For 50 and 90 per cent. benzole

Up to 79° = first runnings.
79° ,, 85° = benzene.
85° ,, 105° = mixed fraction.
105° ,, 115° = toluene.
Remainder = xylene.

For pure benzene

Up to 79° = first runnings.
79° ,, 81° = benzene.
Remainder = last runnings.

For toluene

Up to 109° = first runnings.
109° ,, 110°·5 = toluene.
Remainder = last runnings.

For xylene

Up to 135° = first runnings.
135° ,, 137° = *p*-xylene.
137° ,, 140° = *m*-xylene.
140° ,, 145° = *o*-xylene.
Remainder = last runnings.

Employing this procedure, ordinary commercial benzoles give the following average figures:—

	90 per cent. benzole.	50 per cent. benzole.
First runnings	1·0 per cent.	0·3 per cent.
Benzene	78·8 ,,	18·3 ,,
Middle fraction	10·0 ,,	47·5 ,,
Toluene	8·0 ,,	23·7 ,,
Xylene	2·0 ,,	10·0 ,,
Loss on distillation	0·2 ,,	0·1 ,,

	Pure benzene.	Toluene.
First runnings	0·5 per cent.	0·3 per cent.
Benzene	98·0 ,,	...
Toluene	...	97·3 ,,
Last runnings	1·2 ,,	2·2 ,,
Loss on distillation	0·3 ,,	0·2 ,,

Xylole

First runnings	1·3 per cent.
p-xylene	15·0 ,,
m-xylene	76·5 ,,
o-xylene	5·0 ,,
Last runnings	2·0 ,,
Loss on distillation	0·2 ,,

The separation of the three xylene isomers: *p*-xylene, b.p. 138 4°; *m*-xylene, b.p. 139·2°; *o*-xylene, b.p. 144°, cannot, of course, be completely effected by fractional distillation, but the test is nevertheless of some assistance in estimating the value of a technical xylole as the three isomers differ in commercial utility. According to Jacobsen,[1] commercial tar xylole consists of 70 to 75 per cent. of *m*-xylene, 20 to 25 per cent. of *p*-xylene, and 10 to 15 per cent. of *o*-xylene; its composition varies with the nature of the tar from which it is produced. It also contains up to 10 per cent. of ethyl-benzene,[2] and considerable quantities of paraffin-like substances, which are not attacked by fuming sulphuric acid.

Reuter [3] suggests a method for the estimation of the three xylenes in commercial xylole based upon the fact that sulphuric acid of slightly more than 80 per cent. strength acts upon *m*-xylene to form a sulphonic acid, but has no action on *o*- and *p*-xylene; and that on sulphonating the remaining mixture of *o*- and *p*-xylenes with excess of concentrated sulphuric acid the sulphonic acid of *p*-xylene crystallizes out, whilst that of *o*-xylene remains liquid. A similar method for the determination of *m*-xylene in commercial xylole has been described by Crafts.[4] Börnstein and Kleemann [5] separate the isomeric xylenes by conversion into the xylidines and by their different behaviour with dry sulphur dioxide. Friedel and Crafts [6] have devised a method for the separation of ethyl benzene from *o*-xylene. Manning and Shepherd [7] have examined proposed methods for the determination of the relative proportions of unsaturated and aromatic hydrocarbons and naphthenes of the cyclohexane series in light hydrocarbon oils such as motor benzole. Typical methods are described in papers by Egloff and Morrell,[8] Kattwinkel,[9] Brame [10] and others.[11] These usually depend

[1] *Ber*, 1877, **10**, 1009; 1881, **14**, 2628.
[2] Noelting and Palmer, *ibid.*, 1891, **24**, 1955.
[3] *Chem. Ztg.*, 1889, **13**, 830, 850.
[4] *Compt. rend.*, 1892, **114**, 1110.
[5] *Ber.*, 1891, **24**, Ref. 486.
[6] *Compt. rend.*, 1885, **101**, 1218.
[7] Manning and Shepherd, *Fuel Research Board*, Technical Paper No. 28, 1930.
[8] *Ind. Eng. Chem.*, 1926, **18**, 354.
[9] *Brennstoff-Chem.*, 1927, **8**, 353.
[10] *J. Inst. Petroleum Tech.*, 1926, **12**, 48; Brame and Hunter, *ibid.*, 1927, **13**, 794.
[11] Arnold, *Z. angew. Chem.*, 1923, **36**, 266; Riesenfeld and Bandte, *Erdöl und Teer*, 1926, **2**, 491, 583, 716; 1927, **3**, 139; *Autotechnik*, 1927, **16**, 7; Danaila and co-workers, *Bul. Soc. Romàna Stün.*, 1923, **26** (4-6), 3; *Ann. Mines Roumanie*, 1925, **8**; Faragher, Morrell and Levine, *Ind. Eng. Chem.*, 1930, **2** (Anal.), p. 18.

on noting the successive losses in volume when the oil is treated first with a reagent which absorbs the unsaturated but not the aromatic hydrocarbons and, secondly, with a reagent which absorbs the aromatic but not the saturated hydrocarbons. Less concentrated acids than 80 to 87 per cent. sulphuric acid do not completely remove the unsaturated hydrocarbons; 87 per cent. acid attacks the aromatic hydrocarbons. For the sulphonation and removal of aromatic hydrocarbons the use of 97 to 100 per cent. sulphuric acid and various strengths of fuming acids has been proposed. The lesser concentrations do not effect complete removal except after repeated or very prolonged treatment and fuming acid attacks the saturated hydrocarbons in the acid solution of the sulphonated aromatic compounds. The addition of 2 to 3 per cent. of silver sulphate to the 98 per cent. solution of sulphuric acid was found, by Manning and Shepherd,[1] greatly to accelerate the sulphonation of benzene and its homologues. For the estimation of unsaturated and aromatic hydrocarbons in the same mixture, these investigators employ a nitrating mixture consisting of 16 per cent. of potassium nitrate in 98 per cent. sulphuric acid, a suitable correction being applied for the absorption of any saturated hydrocarbons which may be present. After nitration of a known volume of the sample for two to three hours on the water bath with this nitrating mixture (to which is added a little nitric acid), the mass, after cooling, is poured into excess of water and the nitro-compounds extracted with three separate 50 ml. portions of benzene. The benzene extract is re-extracted with a 10 per cent. solution of sodium hydroxide, washed with water, evaporated to dryness in a tared flask, dried in a current of air at room temperature and finally in a vacuum desiccator. The weight of nitro-compounds so obtained multiplied by 0·455 gives the weight of the corresponding aromatic hydrocarbons in the light oil. Pure benzene, toluene and *m*-xylene give a 96 per cent. conversion into dinitrobenzene, trinitrotoluene and trinitro-*m*-xylene respectively, the respective factors for conversion to yields of aromatic hydrocarbons being 0·484, 0·422 and 0·458 (a mean value of 0·455). Other aromatic hydrocarbons which may be present in light oil yield in general trinitro-derivatives, but only exceptionally do they occur in such an amount as to affect this factor appreciably.

If a more accurate determination of the aromatic hydrocarbons is required, the light oil may be fractionated in an efficient column, cutting at 95° and 124° into three fractions; the aromatic hydrocarbons are then estimated in the three separate fractions as previously described, using the factors 0·484, 0·422 and 0·458 respectively. With light oils low in aromatic hydrocarbons, the oil should first be fractionated to separate the latter and the aromatic hydrocarbons then determined

[1] Manning and Shepherd, *loc. cit.*

	1. Synthetic mixture.		2. Synthetic mixture.		3. Crude low-temperature light oil, 625° C.	4. No. 3 after refining.	5. Power petrol.	6. Light oil, Bergius process.
	Calculated.	Found.	Calculated.	Found.				
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Aromatic hydrocarbons	...	...	7·8	7·8 *	...	32·5	8·9	...
Benzene	39·6	40·2	...	...	8·2 } 24·7	...	...	3·4 } 27·6
Toluene	...	...	...	...	10·7	...	...	6·2
Xylene and higher aromatics	...	...	...	...	5·8	...	...	18·0
Unsaturated hydrocarbons	...	...	12·8	12·3	42·0	28·5	16·8	10·4
Amylene	22·1	21·7	...	...	...	...	...	...
Hexylene	...	...	...	...	...	...	...	...
Saturated hydrocarbons	38·3	38·1	79·4	79·9	33·3	39·0	74·3	62·0
Cyclohexane	...	...	...	...	...	...	...	...
Other saturated hydrocarbons	...	...	...	...	...	...	...	...

* By titration: 8·5 per cent. by weight of nitro-compounds.

by titration of the nitro-compounds with standard titanous chloride solution.

To illustrate the use of the method, data (p. 234) are quoted.

Gooderham [1] describes a modification of the Manning-Shepherd method and apparatus for the analysis of benzoles. The nitrating mixture consists of three volumes of concentrated nitric acid to twenty-five volumes of concentrated sulphuric acid placed in flasks of the design shown in Fig. 41, in amount to seal the top dip tube of the

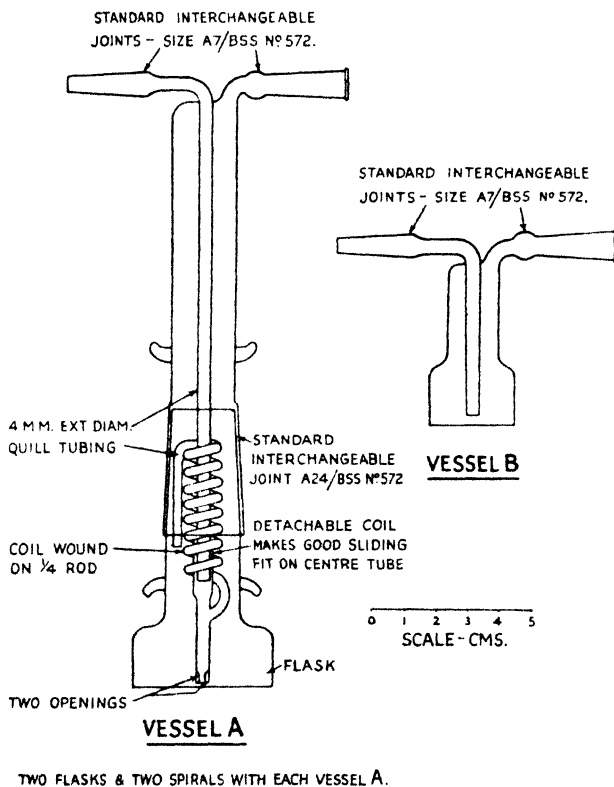



FIG. 41.

spiral. The flasks are weighed, placed in position in the train of apparatus as shown in Fig. 42. About 0·4 g. of benzole is weighed into the tubes U1 and U2. Purified air is drawn through the train of apparatus at a rate controlled by the guard tubes C1 and C2. After the complete evaporation of the benzole, the increase in weight of A1 and A2 allows of the calculation of the percentage of the aromatic plus unsaturated hydrocarbons. From the weight of the unevaporated residue the percentage of gum in the benzole can be obtained. The

[1] *J. Soc. Chem. Ind.*, 1935, **54**, 297 T.

percentage of saturated ("paraffin") hydrocarbons is obtained by difference. The nitration of the aromatic hydrocarbons is then completed as indicated above, but the nitro-derivatives are extracted with five washings (20 to 30 ml. each) of chloroform. After washing the chloroform extract with caustic soda solution and water, the nitro-derivatives are recovered by heating to drive off the chloroform. If a sample of the benzole has been distilled using the modified Dufton column (p. 230), the correct ratio of the three factors (*vide supra*) for conversion to benzene, toluene and xylene respectively are found

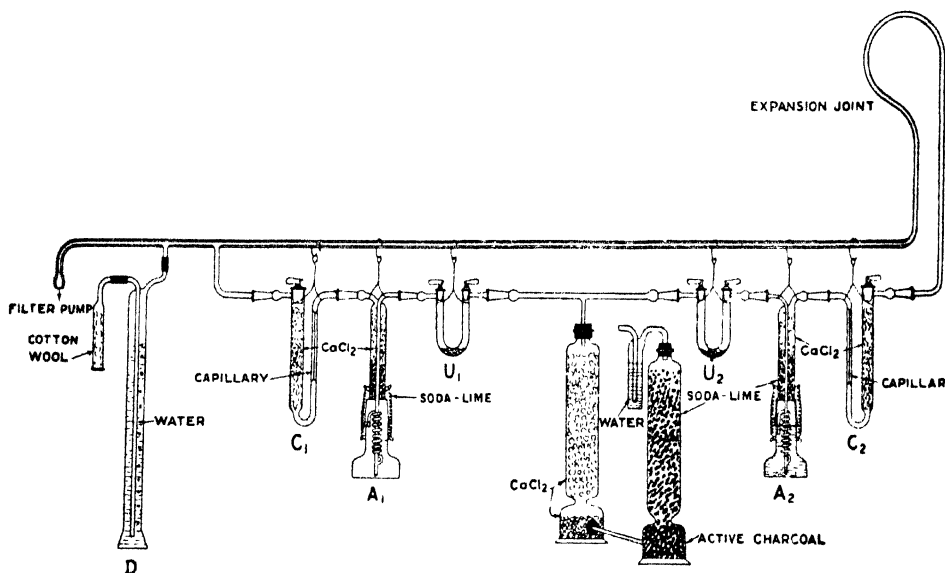



Fig. 42.

from the fractionation graph from the relative amounts of "benzene," "toluene" and "xylene" fractions (*vide infra*). If distillation has not been carried out a mean value of 0·47 is recommended. The table which follows gives characteristic values obtained by this procedure.

When the amounts of unsaturated hydrocarbons or saturated hydrocarbons are large, extraction of nitro-derivatives may become difficult or the saturated hydrocarbons may react slightly with the nitrating mixture. The benzole vapour has then to be passed through two bubblers (Fig. 41, B.) containing 10 to 15 ml. of 70 per cent. by weight sulphuric acid. This strength of acid does not absorb aromatic hydrocarbons but retains the bulk of the unsaturated hydrocarbons. To correct for saturated hydrocarbons reacting with the nitrating mixture in the first bubbler a second bubbler of the same type, containing the same volume of acid, is placed immediately after the first

bubbler. The increase in weight of the second bubbler gives the correction to be applied.

Fractionation							
Benzole.	Per cent. by volume.						
	A.	B.	C.	D.	E.	F.	G.
(*a*) Gas	5·2	2·4	0·5	0·4	2·2	1·1	1·2
(*b*) "Forerunnings," including carbon disulphide, up to 75°	9·3	5·2	0·9	3·8	4·3	5·9	2·6
(*c*) "Benzene" fraction, 75° to 97·6°	78·9	74·0	59·4	54·7	46·6	49·4	36·1
(*d*) "Toluene" fraction, 97·6° to 126·7°	3·1	13·6	23·2	20·2	22·7	19·6	29·0
(*e*) "Xylene" fraction, 126·7° to 165°	0·3	3·3	10·8	8·9	14·2	12·6	26·8
(*f*) 165° to 205° } Residue	0·7	1·5	4·8	5·8	8·2	5·3	3·6
(*g*) Boiling above 205° } Residue	2·5	nil	0·4	6·2	1·8	6·1	0·7
Approximate amount of pure constituent by fractionation							
Benzene	75	67	57·5	50	37	39	†
Toluene	1	4*	20	16	16	7	†
Xylene	nil	1	9	7	9	8	†
Manning-Shepherd Method							
	Per cent. by weight.‡						
Aromatic hydrocarbons	81·9	91·4	90·7	73·2	67·6	69·0	64·8
Unsaturated hydrocarbons	9·8	3·5	6·9	9·6	17·4	10·2	18·6
Saturated hydrocarbons	8·1	4·2	2·3	15·6	14·4	17·9	15·7
Gum	0·2	0·9	0·1	1·6	0·6	2·9	0·9

* At 108·5° = 7 per cent. † Contains many other compounds.
‡ Specific gravities of aromatic hydrocarbons, unsaturated hydrocarbons and saturated hydrocarbons may be assumed to be 0·87, 0·82 and 0·77 respectively.

Reichel [1] describes a somewhat similar method for the quantitative estimation of *m*-xylene in commercial benzoles and benzole mixtures, which depends upon the fact that vigorous nitration of *m*-xylene with concentrated nitric acid, or with a mixture of nitric acid of sp. gr. 1·5 and concentrated sulphuric acid of 66° Bé gives, quantitatively, 2 : 4 : 6-trinitro-*m*-xylene (m.p. 182°), which is soluble in acetone with difficulty. *p*-Xylene, however, under these nitration conditions, gives 2 : 3 : 5-trinitro-*p*-xylene (m.p. 140°) which is readily soluble in acetone, whereas little solid nitration product is formed from *o*-xylene.

Reichel's method has been adopted as the Standard Method for the determination of *m*-xylene in commercial xyloles (see p. 253).

According to Weber,[2] benzole, toluole and xylole can be detected

[1] *Chem.-Ztg.*, 1931, **55**, 744.
[2] *Ibid.*, p. 201.

by testing their nitration products in alkaline solution with isoamyl-alcohol, benzyl alcohol and cyclohexanol, with which they give characteristic colour reactions.

Finally Jacobsen [1] has described a method of separation of the isomeric trimethyl benzenes which depends upon the different behaviour of their sulphamides towards alcohol.

2. **Standard Commercial Analysis.**—Technical methods of analysis of light coal-tar products for the estimation of benzene, toluene and xylene, and for the estimation of the impurities present (carbon disulphide, thiophen and paraffins, including naphthenes) have been standardized by the Standardization of Tar Products Tests Committee.[2] In general these methods depend on fractional distillation, and the change in sp. gr. after the removal of impurities. They are as follows :—

(a) *The Determination of Benzene, Toluene and Xylene, Carbon Disulphide and Paraffins, including Naphthenes.*

The following Standard Method of analysis [3] is only applicable to samples which have previously been washed with sulphuric acid to remove unsaturated hydrocarbons. Unwashed samples must first be washed with 95 per cent. sulphuric acid as indicated on p. 181 ; the loss on washing is noted and allowed for in the calculation of the results. Fractionation is varied according to the composition of the washed oil. When not less than 45 per cent. distils under the prescribed conditions below 90° the fractions collected directly are as follows :—

(*a*) Up to 90° : This fraction contains only benzene and toluene together with carbon disulphide and low-boiling paraffins ;
(*b*) 90 to 140° : This fraction consists of benzene, toluene and xylene with paraffins of similar boiling point ;
(*c*) 140° to 160° : This fraction consists of xylenes, cumenes, etc., with paraffins ;
(*d*) 160° to 190° : This fraction consists of higher homologues of benzene with some paraffins, and
(*e*) Residue at 190° which consists chiefly of polymerized hydrocarbons.

When the amount boiling below 90° is less than 45 per cent., small amounts of xylene may distil over with the benzene and toluene below 90° ; the first fraction is taken accordingly up to 95°, refractioned up to 90°, and the residue containing all the xylene added to the second fraction from 95° to 140°. When the proportion of xylene and higher boiling constituents is low, it is often not possible to continue the distillation up to 140°, owing to their vapours all condensing in the fractionating column. In such cases xylene is added to the residue

[1] *Ber.*, 1876, **9**, 256.
[2] *Standard Methods for Testing Tar and Its Products*, London, 1938.
[3] Colman and Yeoman, *J. Soc. Chem. Ind.*, 1919, **38**, 57 T.

above 90°, and the distillation continued up to 140°; the determination of the fractions 140° to 160°, 160° to 200°, and residue is omitted, or a larger quantity of the original oil must be taken.

When mixtures of benzene and toluene are distilled from a distillation flask under the specified conditions, the percentage of distillate at any given temperature is constant. If the volume of distillate from 100 ml. of the mixture to any temperature is determined for a definite rate and for a definite size of fractionating flask, then with an unknown mixture of benzene and toluene the percentages of benzene and toluene can be found by comparing the volume of distillate obtained under the same conditions with that found in the case of mixtures containing known amounts of the two constituents.[1] The results obtained with pure mixtures are most conveniently presented in graph form, the percentages of toluene being plotted as ordinates and the percentages of distillate as abscissae (Graph 3). The percentage of benzene is found by difference. When carbon disulphide and paraffins are absent, the reading obtained from the graph gives directly the percentage of benzene and toluene in the sample. When the above-named impurities are present, from the sp. gr. of the sample before and after removal of the carbon disulphide, the percentage of carbon disulphide present may be calculated,[2] applying a correction for the expansion which occurs on mixing carbon disulphide with benzene or mixtures of benzene and toluene.[3] Graph 5 (p. 242) has thus been compiled. In like manner the percentage of paraffins is calculated from the observed sp. gr. of the sample after removal of carbon disulphide, and the sp. gr. which a sample containing the percentage of toluene found would have if paraffins were absent; no material expansion occurs on mixing benzene and toluene with the amount of the latter found in the fraction up to 90°, or in commercial benzole. Expansion occurs on mixing paraffins with benzene or mixtures of benzene and toluene and accordingly a correction must be applied. The sp. gr. of the paraffins present may be taken without material error as 0·730 in the former products. From the observed sp. gr. of the sample after removal of carbon disulphide and the percentage of toluene found by Graph 3, the percentage of paraffins in the sample after removal of carbon disulphide is read off directly from Graph 7.

(1) *Preliminary Distillation.* Five hundred ml. of the washed sample (or not less than 250 ml. if 500 ml. are not available) is distilled at the rate of about 5 ml. per minute in a round-bottomed metal or glass flask of suitable capacity, fitted with a standard 12-bulb pear column.

[1] James, *J. Soc. Chem. Ind.*, 1916, **35**, 236.

[2] Nickels, Allen's *Commercial Organic Analysis*, London, 4th edn., 1914, vol. iii., p. 228; Spielmann and E. G. Wheeler, *J. Soc. Chem. Ind.*, 1916, **35**, 396.

[3] F. D. Brown, *J. Chem. Soc.*, 1879, **35**, 552; 1881, **39**, 2051.

The following fractions are collected, without interruption of the distillation, and measured separately :—Up to 90°, 90° to 140°, 140° to 160°, 160° to 190°, and residue at 190°. When the amount distilling below 90° is less than 45 per cent. of the total, the first fraction is taken up to 95°, and the second from 95° to 140°; the first fraction is then redistilled in the same manner, the fraction up to 90° collected and the residue added to the 95° to 140° fraction, this mixture then forming the true second fraction. The fractions so obtained from samples containing little or no carbon disulphide or paraffins are examined according to Part I below; if these materials are present in material amount, corrections are made according to the methods given in Part II.

(2) PART I—**Carbon disulphide and paraffins absent or present only in very small quantities.**

(a) *Fraction up to* 90°. This procedure is also suitable for the direct analysis of 90's benzole.

100 ml. of the fraction is distilled at the rate of 7 ml. per minute in a standard distillation flask fitted with a standard thermometer having a range of 70° to 130°, and connected to a water-cooled condenser which drains completely. Corrections are applied for barometric pressure (p. 134). The distillate is received in a standard graduated cylinder of suitable capacity. Distillation is continued until the temperature reaches 85° (corrected), when the flame is extinguished, the condenser allowed to drain completely, and the amount of distillate read off. If the sample should contain more than 20 per cent. of toluene, however, distillation is best continued to 90° (corrected) and the distillate at that temperature measured. The percentage of toluene is read off on Graph 3, that of the benzene being found by difference. From the amounts of benzene and toluene in 100 ml. of the fraction, the quantities present in the whole of the fraction are calculated by proportion.

In commercial 90's benzole small amounts of xylene are usually present as well as toluene and the toluene figure determined as above represents the percentage of toluene plus xylene. If an estimation of the latter is desired, the sample is distilled through a standard 12-bulb pear column into a fraction up to 90° and a fraction over 90°, the first fraction being analysed as above, and the second in the manner described below for the 90° to 140° fraction.

(b) *Fraction from* 90° *to* 140°. This procedure is also suitable for the direct analysis of commercial toluole.

100 ml. of the fraction is distilled at the rate of 7 ml. per minute, using the same distillation apparatus as in (*a*), and applying the usual corrections for barometric pressure. When the temperature reaches 105° (corrected), the flame is extinguished, the condenser allowed to drain completely, and the volume of distillate measured. Distillation is now continued at the same rate up to 116° (corrected), the flame again extinguished, and the amount distilling from 105° to 116° measured. The cooled residue in the flask is also measured; the sum of the three fractions so obtained must not be less than 99·5 ml. The volumes of the 100 ml. first taken and of the fractions obtained must be read at the same temperature. Graph 4 holds good only for such mixtures of benzene, toluene and xylene as contain not more than 75 per cent· of toluene and give more than 5 per cent. of distillate below 105°, and 5 per cent. boiling above 116°. When the mixture gives figures which

show no reading on the graph, the procedure is modified by taking for analysis a smaller amount than 100 ml. and adding known amounts of pure benzene, pure toluene or pure xylene (boiling from 138° to 143°). The quantities of these which it is necessary to add depend upon the composition of the sample and must be chosen according to judgment, but the following may be taken for guidance :—

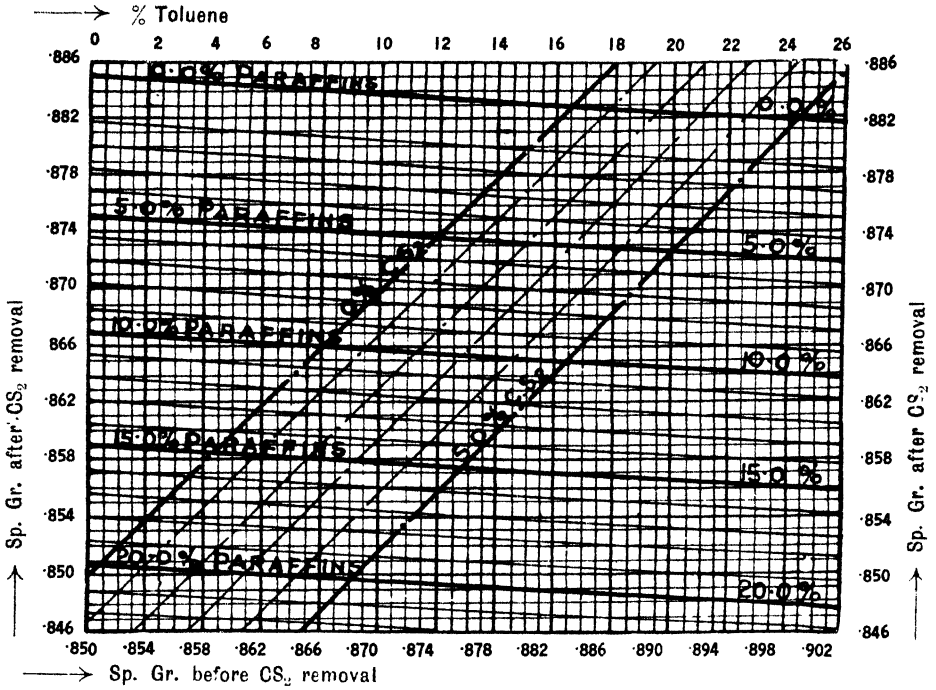
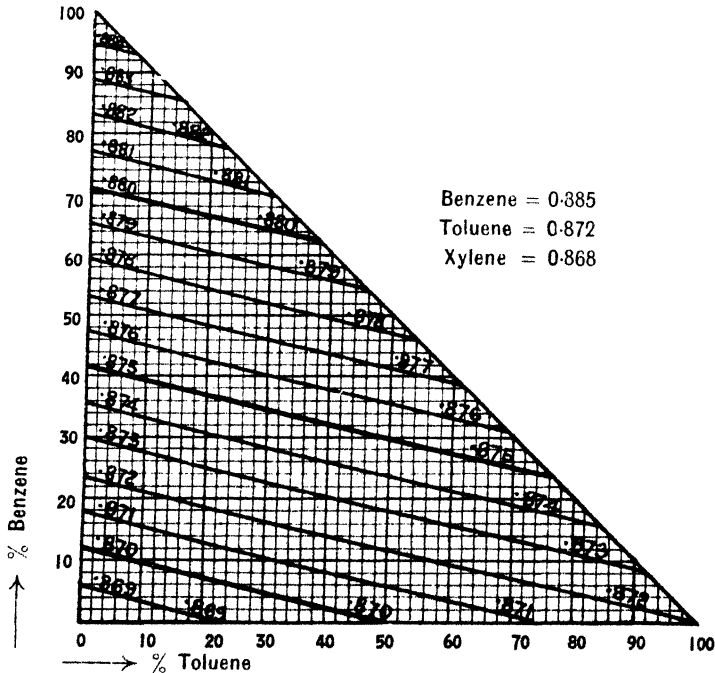
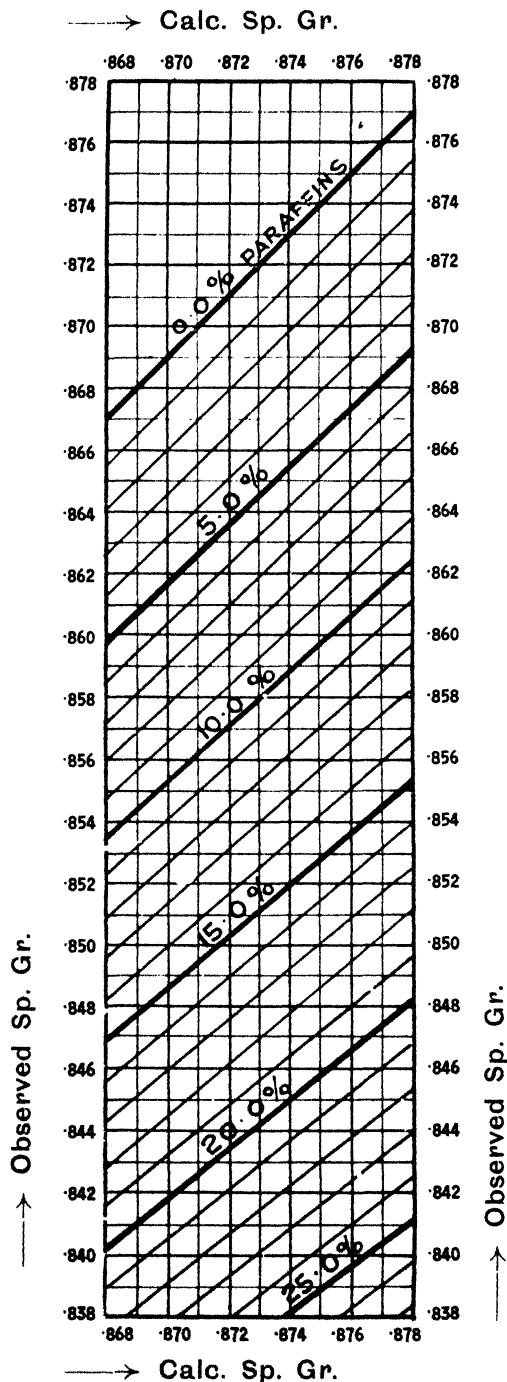
For the fraction 90° to 140°, obtained as above, it usually suffices to take 80 ml. of the fraction and add 20 ml. of toluene, in order to give a mixture, the volumes of distillates from which fall within the limits of Graph 4. From the results of the analysis of such a mixture of 80 ml. of the fraction plus 20 ml. of toluene, the composition of the original fraction is calculated as follows :—

Mixture of 80 ml. fraction and 20 ml. toluene yielded.		Deduct amount added to mixture.	Amount in 80 ml. of fraction.	Amount in 100 ml. of fraction.	Percentage in fraction.
Benzene . . .	28·0 ml.	0·0 ml.	28·0 ml.	$\frac{28\cdot0 \times 100}{80}$	= 35·0
Toluene . . .	56·0 „	20·0 „	36·0 „	$\frac{36\cdot0 \times 100}{80}$	= 45·0
Xylene . . .	16·0 „	0·0 „	16·0 „	$\frac{16\cdot0 \times 100}{80}$	= 20·0

From the percentage composition of the fraction, the volumes of benzene, toluene and xylene in the total volume of the fraction 90° to 140° is found by proportion. The sum of the volumes of benzene and toluene respectively found in the fractions up to 90° and 90° to 140° gives the total volumes of benzene and toluene in the volume of the sample taken for analysis.

Samples of 50/90's benzole are fractionated through a standard 12-bulb pear column into the portions distilling up to 90° and above 90°, each of which is separately analysed according to (*a*) and (*b*) above.

When commercial toluole gives results which do not fall on the graph, a mixture of 75 ml. of the sample with 15 ml. of benzene and 10 ml. of xylene usually provides a mixture of suitable composition for distillation. For example, a sample of 75 ml. of a commercial toluole, to which 15 ml. of benzene and 10 ml. of xylene had been added, gave 21·8 per cent. of distillate up to 105° and 29·0 per cent. of residue at 116°. From Graph 4 the sample therefore contained benzene, toluene and xylene in the proportions shown below (column 5) :—

Mixture of 75 ml. of sample, 15 ml. of benzene, and 10 ml. of xylene yielded.		Deduct amount added to sample.	Amount in 75 ml. of sample.	Amount in 100 ml. of sample.	Percentage in sample.
Benzene . . .	**21·0 ml.**	**15·0 ml.**	**6·0 ml.**	$\frac{6\cdot0 \times 100}{75}$	**= 8·0**
Toluene . . .	**60·0 „**	**0·0 „**	**60·0 „**	$\frac{60\cdot0 \times 100}{75}$	**= 80·0**
Xylene . . .	**19·0 „**	**10·0 „**	**9·0 „**	$\frac{9\cdot0 \times 100}{75}$	**= 12·0**

GRAPH 5.—Percentage of Carbon Disulphide and Paraffins in Fraction "up to 90° C." and in 90's Benzole.

GRAPH 6.—Calculated Specific Gravity of Paraffin-free Mixtures of Benzene, Toluene and Xylene

GRAPH 7.—Percentage of Paraffin in Fraction "90° to 140° C." and in Commercial Toluole.

(c) *Fraction from* 140° *to* 160°. This fraction consists entirely of the constituents of solvent naphtha.

To the amount of this fraction is added a quantity of xylene found in the fraction from 90° to 140°, the combined volume representing the volume of "solvent naphtha free from toluene," contained in the volume of the sample taken for analysis.

For the determination of benzene and toluene in washed solvent naphtha, 100 ml. of the sample is fractionated through a standard 12-bulb pear column and the distillate to 138° collected in a 100 ml. receiver.

To this is added 20 ml. of pure benzene and the quantity of pure toluene necessary to make up the contents to 100 ml. The mixture is then distilled as above for commercial toluene and the percentages of benzene and toluene in the mixture ascertained by Graph 4 from the percentages boiling up to 105° and above 116°. The percentage of benzene so found, less the 20 ml. added and that of toluene less the amount of pure toluene added, give directly the percentages of benzene and toluene respectively in the original solvent naphtha.

(d) *Fraction from* 160° *to* 190° (*Heavy Solvent Naphtha*). This fraction consists entirely of the constituents of heavy solvent naphtha and the volume of the fraction found is taken as that of heavy naphtha in the volume of the sample taken for analysis.

(3) PART II—**Correction for carbon disulphide and paraffins including naphthenes when these are present in material amount**

The fraction up to 90° may contain both carbon disulphide and paraffins and the higher fractions may contain paraffins. Corrections in respect of these constituents are made, by means of sp. gr. determinations, as set out below :—

(a) *Fraction up to* 90°. This procedure is also available for the direct analysis of 90's benzole.

The sp. gr. of the fraction at 15·5°/15·5° is determined accurately to the third decimal place. 100 ml. of the fraction (or if the quantity available is limited, of the combined residue and distillate from the distillation to 85° or 90° previously made for the determination of the toluene content) is mixed with 50 ml. of alcohol or industrial methylated spirit free from paraffins and pyridine ; 5 g. of solid sodium hydroxide is added and the whole shaken for five minutes. 200 ml. of water is then added with renewed shaking ; after settlement, the lower aqueous layer is run off, the upper layer washed with two successive quantities of 25 ml. of water and dried with calcium chloride.

The sp. gr. of the dried spirit at 15·5°/15·5° is then taken accurately to the third decimal place. From the sp. gr. of the spirit before and after removal of carbon disulphide, the percentage of the latter is found from Graph 5 (p. 242). From the percentage volume of toluene previously found in the fraction by distillation to 85° or 90°, and the sp. gr. of the spirit after removal of carbon disulphide, the percentage of paraffins in the fraction is read off on the same graph.

(b) *Fraction from* 90° *to* 140°. This procedure is also available for the direct analysis of commercial toluole.

The sp. gr. of the fraction at 15·5°/15·5° is ascertained accurately to the third decimal place. From Graph 6 (p. 242) the calculated sp. gr. of the mixture of benzene, toluene and xylene free from paraffins is ascertained, knowing the percentages of benzene and toluene in the fraction from the analyses made in Part I. above. From the sp. gr. of the fraction and the calculated sp. gr. the percentage of paraffins in the fraction is read off on Graph 7 (p. 243).

(c) *Fraction from* 140° *to* 160°. Only an approximate estimate of the paraffins in this fraction is possible by sp. gr. determinations, because of the varying composition of the aromatic hydrocarbons contained in it. Such an approximation is

made on the assumption that the sp. gr. of the solvent naphtha free from paraffins is 0·868, while that of the paraffins present is 0·760. The percentage (x) of paraffins is found from the equation :—

$$0{\cdot}760x + 0{\cdot}868(100 - x) = 100\ S.$$

or,

$$x = \frac{86.8 - 100\ S}{0{\cdot}108}$$

where S is the sp. gr. at 15·5°/15·5° of the fraction from 140° to 160°.

The results thus obtained are usually within two to three units of the true value and within one to two units when the paraffin percentage is not more than about 25.

(d) *Fraction from* 160° *to* 190°. The varying proportions of coumarone and indene render impracticable even an approximate estimation of the paraffin percentage by observation of the sp. gr. If the paraffin content is required it can best be determined by a sulphonation method (p. 267).

The following example is taken from the original paper by Colman and Yeoman (*loc. cit.*) :—

Analysis of crude benzole from vertical retorts

Volume taken for analysis = 500 ml. Sp. gr. at 15·5° = 0·854.

Original Sample.		*Unwashed Fraction to 200°.*	
Distillate to 200°	462 ml.	Volume after alkali washing	458 ml.
		Loss	4 ,,
Residue at 200° (diff.)	38 ,,	Volume after acid washing	420 ,,
		Loss	38 ,,

Fractionation of Washed Distillate

Up to 90°	160 ml.	Sp. gr. 0·856
90° ,, 140°	147 ,,	,, 0·840
140° ,, 160°	37 ,,	,, 0·824
160° ,, 200°	30 ,,	,, 0·840
Residue at 200° (by diff.)	46 ,,	...

Washed Distillate up to 90°

100 ml. gave 83·3 ml. up to 85° (uncorrected).
From Graph 3. Benzene = 90 per cent. (uncorrected).
Toluene = 10 per cent.
Sp. gr. before carbon disulphide removal = 0·856.
,, ,, after ,, ,, ,, = 0·854.
From Graph 4. Carbon disulphide = 0·5 per cent.
Paraffins = 17·2 per cent.

	Percentage composition of fractions.	Composition of 160 ml.
Carbon disulphide	0·5	0·8 ml.
Paraffins	17·2	27·5 ,,
Benzene	74·1	118·6 ,,
Toluene	8·2	13·1 ,,

Washed Distillate 90° *to* 140°

81 ml. + 19 ml. toluene + 0 ml. benzene.

			From Graph 4.
Up to 105° . .	39·8 per cent.	Benzene .	29·3 per cent.
105° „ 116° . .	35·3 „	Toluene .	53·6 „
Above 116° . .	24·5 „	Xylene . .	17·1 „

	In 81 ml. of washed distillate, 90° to 140°.	In 100 ml. of washed distillate, 90° to 140°.
Benzene (uncorrected)	29·3	36·2
Toluene „	34·6	42·7
Xylene „	17·1	21·1

Sp. gr. of fraction = 0·840.
Calculated sp. gr. of paraffin-free sample from Graph 6 = 0·876.
Therefore, from Graph 7, paraffins = 24·7 per cent.

	Percentage composition of fraction.	Composition of 147 ml of fraction.
Paraffins	24·7	36·3
Benzene	27·2	40·1
Toluene	32·2	47·3
Xylene	15·9	23·3

Summarizing:

	Total in 500 ml. of original sample.	Percentage of original.	
Carbon disulphide . .	0·8	0·2	
Paraffins to 140° . .	63·8	12·8	
Benzene	158·7	31·7	
Toluene	60·4	12·1	
Solvent naphtha . .	60·3	12·0	Approx. 40 to 45 per cent. paraffins.
Heavy naphtha . .	30·0	6·0	
Loss on alkali washing .	4·0	0·8	
Loss on acid washing .	38·0	7·6	
Above 200° washed distillate . . .	46·0	9·2	
Above 200° in original .	38·0	7·6	

(b) *Alternative Method.*[1] (*Not accepted as a British Standard Method*)

Estimation of benzene and toluene in samples free, or almost free, from paraffins may be rapidly approximated by distillation through a 5-ft. Dufton column. The column is ¾ in. internal diameter fitted internally with tubes increasing from ½ in. at the bottom to ⅝ in. at the top, and wound in sections with nickel wire from 14 S.W.G. at the bottom to 18 S.W.G. at the top, the wires being spaced upwards from 1 in. to ½ in. 200 ml. of the sample (*e.g.* a benzole) is treated in a 350-ml. round-bottomed flask to which the Dufton column is attached, the rate of distillation not exceeding one drop per second.

[1] Hoffert and Claxton, *Motor Benzole, Its Production and Use*, London, 1931, p. 604; *cf.* Washburn, *U.S. Bureau of Standards*, Technical Paper No. 140, 1919.

To prevent priming, the column is lagged, except for 6 in. at the top, and also wound electrically with nichrome wire, so that it may be electrically heated. By plotting the volumes of the percentages distilling against the temperature, the percentages of benzene (up to 95°) and toluene (95° to 125°) may be obtained ; the difference between one hundred and the sum of these represents the xylenes and higher boiling aromatic constituents. To estimate the latter, a measured volume of a high-boiling liquid may be added to the sample before fractionation and distillation can be carried above 125°.

(c) *The Determination of Carbon Disulphide, Thiophen, Toluene and Paraffins including Naphthenes in Commercially Pure Benzole*

A method devised by Butler-Jones [1] was standardized in *Standard Methods*, 1929. The test is not in general use or demand but where a standard method is required, the 1929 technique is appropriate. It is described below. The method is only applicable to samples which, on washing with 10 per cent. by volume of 90 per cent. sulphuric acid, give not more than a pure lemon-coloured acid layer. Otherwise the sample must be washed, with successive quantities if necessary of 5 per cent. by volume of cold 90 per cent. sulphuric acid, separated, washed with alkali until freed from acid, and then with water until free from alkali. If appreciable diminution in volume occurs the extent of the diminution must be measured and allowed for.

The crystallizing point of the original sample (C.P.1) is determined. The carbon disulphide is then removed completely with alcoholic potash, and the crystallizing point redetermined (C.P.2). Thiophen is now removed using Denigès reagent, and the crystallizing point (C.P.3) and the sp. gr. at 15·5°/15·5° ascertained. The percentage of carbon disulphide is proportional to the difference between C.P.1 and C.P.2, and the percentage of thiophen to the difference between C.P.2 and C.P.3. The amount by which C.P.3 is below that of pure benzene is a measure of the sum of the percentages of paraffin and toluene, as is also the amount by which the sp. gr. of the washed sample is below that of pure benzene. The equations relating the above determinable constants and the volume percentages of the four solutes are solved graphically, so that the volume percentages may be read off directly. The crystallizing points are determined in an efficient crystallizing point apparatus, provided with a Beckmann thermometer. The reading of the thermometer at 0° is determined. The bulb of the thermometer should be approximately equidistant from the bottom and sides of the tube containing the sample and only a little more than covered by the liquid. Cooling agents giving temperatures below 0° must not be used. The

[1] *J. Soc. Chem. Ind.*, 1918, **37**, 324 T.

crystallizing point (A) of the sample is first determined. Carbon disulphide is then removed from the sample by shaking 60 to 70 ml. with 10 ml. of 10 per cent. alcoholic potassium hydroxide or sodium hydroxide solution in a stoppered bottle for one hour. The alcohol must be pure ethyl alcohol (which need not be absolute) or industrial methylated spirits free from paraffins and pyridine. The mixture is transferred to a separating funnel and extracted three times with cold water, at least 200 ml. of water being used for the first extraction, and smaller quantities for the second and third. The crystallizing point (B) of the washed liquid is then determined. The percentage by volume of carbon disulphide in the sample is $\frac{B-A}{0{\cdot}94}$.

Thiophen is now removed by shaking 30 to 40 ml. of the sample, purified as above, with twice its volume of Denigès reagent in a stoppered bottle for three hours. The residual benzole is transferred to a separating funnel, washed twice with cold water, and finally filtered through a small filter paper in a covered funnel. It is advisable at this stage to determine the complete removal of the thiophen by submitting the benzole to the isatin test (p. 263). The crystallizing point of the sample is now determined (C). The percentage by volume of thiophen in the original sample is $\frac{C-B}{0{\cdot}465}$.

The sample is then dried by means of a pellet of fused calcium chloride and the sp. gr. (D) at $15{\cdot}5^\circ/15{\cdot}5^\circ$ determined as accurately as possible to the fourth place of decimals. The percentage of toluene and paraffins in the original sample is read off from Graph 8 (opposite) or determined from the following simultaneous equations :—

$$5{\cdot}48-C = 0{\cdot}52 \times \text{toluene} + 0{\cdot}425 \times \text{paraffins}.$$
$$0{\cdot}8848-D = 0{\cdot}0001 \times \text{toluene} + 0{\cdot}0008 \times \text{paraffins}.$$

Soap must be used to lubricate the taps of the separating funnels; grease must not be used.

(d) *The Determination of Benzene, Toluene and Xylene in Pure and Commercial Toluole*

For the determination of benzene, toluene and xylene in products which contain from 50 to 100 per cent. of toluene, the method described by Northall-Laurie[1] was adopted as the Standard Method in 1929 (but see p. 253). If a sample contains less than 50 per cent. of toluene as, for example, 50/90's benzole, a known volume of pure toluene is added in sufficient quantity to bring the results within the range of

[1] *Analyst*, 1915, 40, 384.

the determined data shown in Graph 9 (facing p. 248) ; thus, 100 ml. of pure toluene is added to 100 ml. of the sample before making the determination. The method is dependent upon the boiling-points of mixtures of benzene and toluene of known composition.

200 ml. of the sample, measured at tap-water temperature, is placed in a distillation flask of just sufficient capacity to distil 200 ml. and fitted with an efficient condensing system. The neck of the flask should extend only a short distance above the side tube. Distillation is then commenced at the uniform rate of 7 ml. per minute into a 50 ml. standard Crow receiver (No. V 2, p. 438), until 50 ml. has collected. The receiver is then immediately replaced by a 100 ml. standard Crow receiver (No. V 1, p. 438) without stopping the distillation. When a further 98·5 ml. has been collected, the flame is extinguished and the flask allowed to cool. Drainage will account for a collection of 100 ml. The distillate must fall into the receiver at tap-water temperature. The first 50 ml. should be dried with a pellet of fused calcium chloride. The residue in the flask, after cooling the flask under the tap, is transferred to a standard boiling-point flask (No. B 1, p. 450). The flask is fitted with a standard thermometer of range, 80° to 140° (No. T 10*a*, p. 436), so that the bulb is entirely within the glass cylinder fused in the neck of the flask. The flask is supported 3¼ in. (83 mm.) above the top of a Bunsen burner, which must be screened from draught by means of a cylinder of wire gauze ; the flask rests on a square of asbestos having a central hole 1¼ in. (32 mm.) in diameter. The thermometer must be screened by means of a square of cardboard or asbestos slipped over the cork in the neck of the flask. A second thermometer is suspended within 3 in. (75 mm.) of the first thermometer to give the air temperature immediately surrounding the stem of the latter. Finally the whole apparatus should be well protected from draughts.

The contents of the flask are boiled at such a rate that the condensate runs back at the uniform rate of one drop per second ; a metronome is best used to regulate this rate. After ten minutes, when the temperature becomes constant, the temperature is noted and corrected for atmospheric pressure and length of emergent stem (*vide infra*). The boiling point of the first 50 ml. is determined in a similar manner and likewise corrected. The percentages of benzene and toluene in the sample are read off directly from Graph 9 (facing p. 248). The percentage of xylene is represented by the difference between 100 and the sum of the percentages of benzene and toluene.

The following corrections are applied :—

1. **Barometric pressure.** The following corrections apply within the usual limits encountered :—

Correction of temperature readings for barometric pressure

Pressure. mm.	Correction. °C.	Pressure. mm.	Correction. °C.	Pressure. mm.	Correction. °C.
770	−0·45	759	+0·05	748	+0·55
769	−0·40	758	+0·10	747	+0·60
768	−0·35	757	+0·15	746	+0·65
767	−0·30	756	+0·20	745	+0·70
766	−0·25	755	+0·20	744	+0·75
765	−0·20	754	+0·25	743	+0·80
764	−0·20	753	+0·30	742	+0·85
763	−0·15	752	+0·35	741	+0·90
762	−0·10	751	+0·40	740	+0·90
761	−0·05	750	+0·45	739	+0·95
760	0·00	749	+0·50	738	+1·00

2. Emergent stem of thermometer. Corrections to be added for various lengths of emergent stem, allowing for the number of exposed degrees (N) and the difference between the observed boiling point (T) and the temperature (*t*) indicated by the thermometer outside the flask, are given below (*cf.* p. 134) :—

Corrections of the thermometer readings for emergent stem (corrections to be added)

N.	(T−*t*) °C.						
	50°.	60°.	70°.	80°.	90°.	100°.	110°.
10	0·07	0·09	0·10	0·12	0·13	0·14	0·16
20	0·15	0·17	0·20	0·23	0·26	0·29	0·32
30	0·22	0·26	0·30	0·34	0·39	0·43	0·48
40	0·29	0·35	0·40	0·46	0·52	0·57	0·63
50	0·36	0·43	0·50	0·57	0·65	0·71	0·79
60	0·43	0·52	0·60	0·68	0·78	0·86	0·95
70	0·50	0·60	0·70	0·80	0·91	1·00	1·10
80	0·57	0·69	0·80	0·91	1·03	1·14	1·27
90	0·65	0·77	0·90	1·02	1·17	1·29	1·42
100	0·72	0·86	1·00	1·14	1·30	1·43	1·57

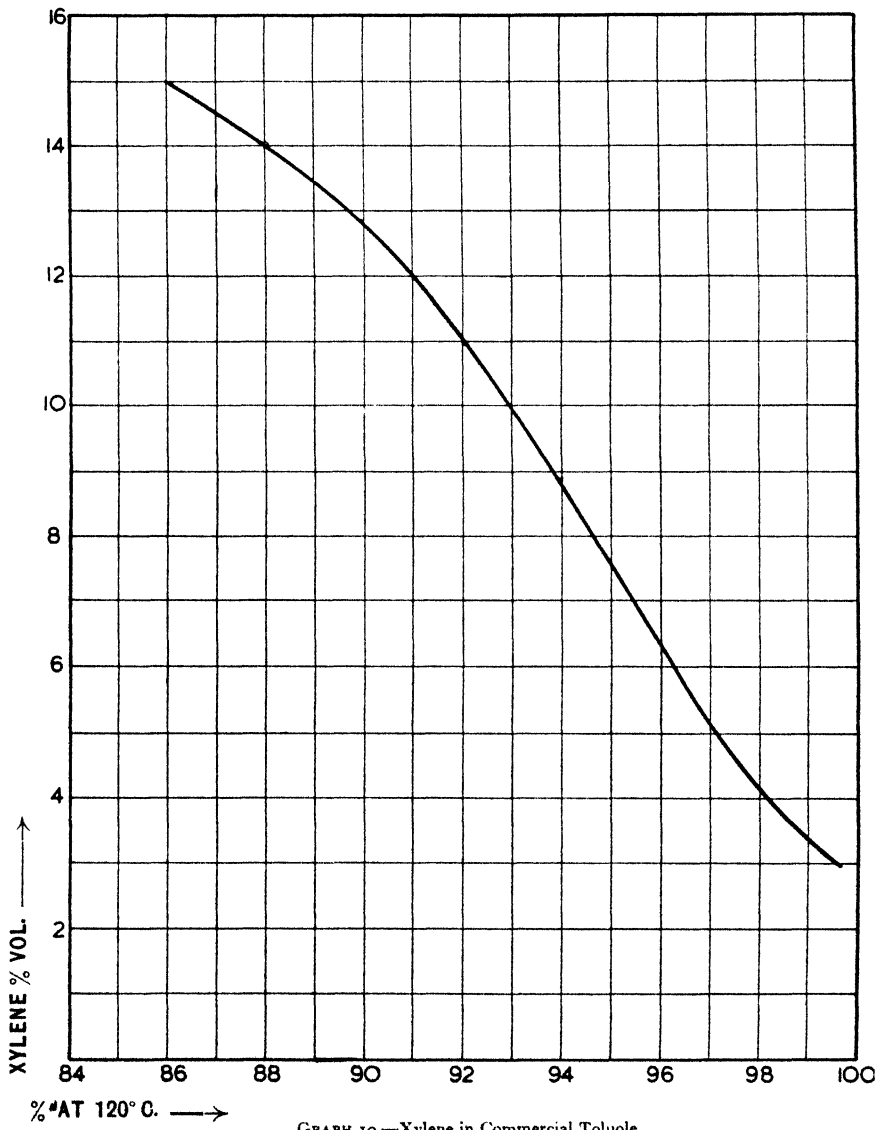
3. **Corrections for paraffins (including naphthenes).**—Any paraffins in the sample appear in the analysis as benzene, toluene and xylene. The percentage of paraffins present in toluoles containing 90 per cent. or more of toluene may be found with a fair degree of accuracy from the difference between the sp. gr. of the sample at 15·5°/15·5° and that (0·872) of pure toluene at the same temperature. Each 0·001 in the sp. gr. of the sample below 0·872 represents approximately 0·66 per cent. of paraffins in the sample. If the amount of toluene is less than 90 per cent. the proportion of paraffins may be ascertained from the uncorrected percentages of benzene, toluene and xylene found and the observed sp. gr. of the sample as described on p. 244. Alternatively, the percentage of paraffins may be determined by sulphonation (p. 267).

Example:

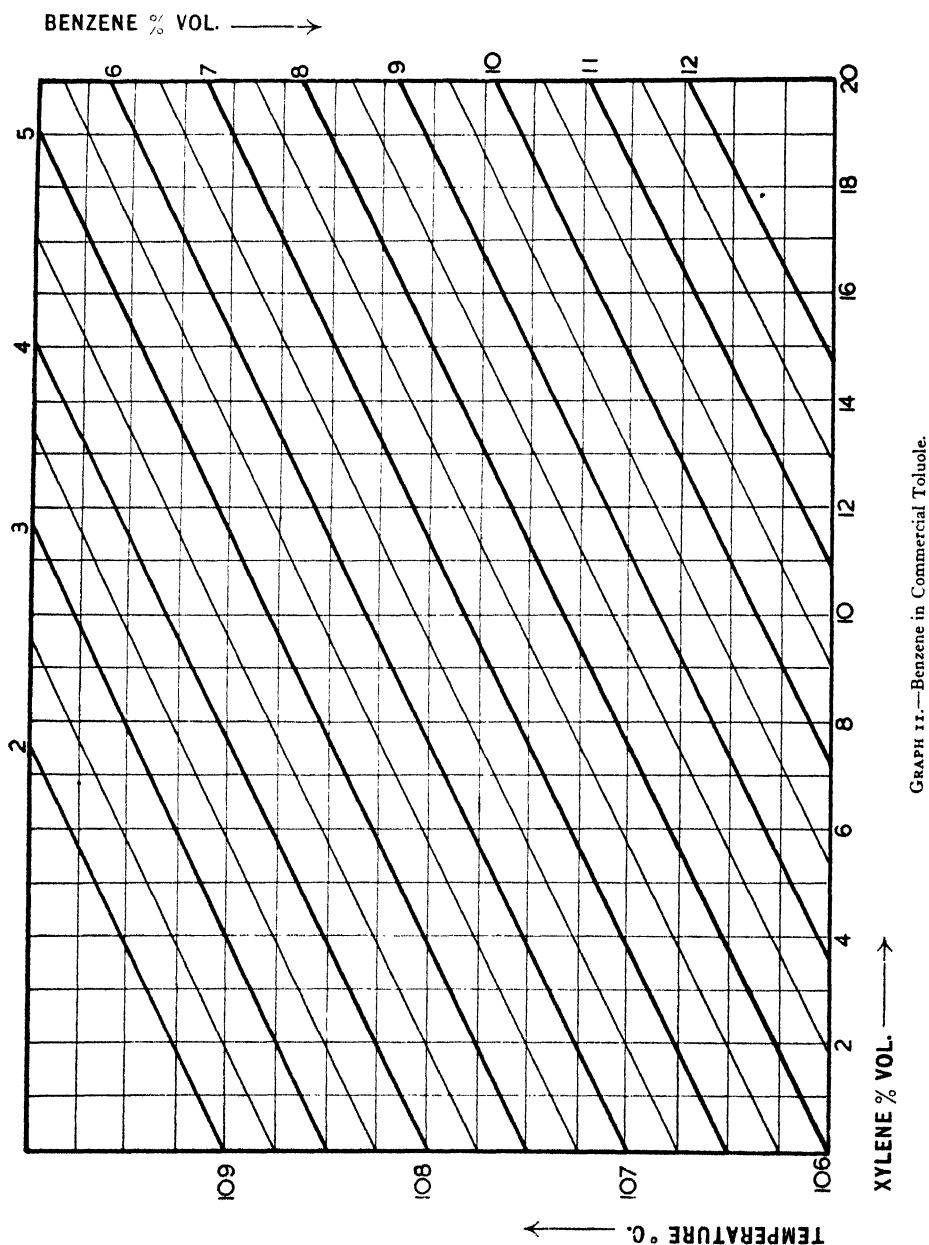
Found, percentages of benzene, toluene and xylene, 20, 75 and 5 respectively. Observed sp. gr. of sample 0·867. Percentage of paraffins found to be 4 according

to method described on p. 244. Then percentages of paraffin-free benzene, toluene and xylene are found by multiplying the uncorrected percentages by

$$\frac{100-4}{100} = 0{\cdot}96.$$

i.e.			
Benzene corrected for paraffins	= 20×0·96	= 19·2	per cent.
Toluene ,, ,, ,,	= 75×0·96	= 72·0	,,
Xylene ,, ,, ,,	= 5×0·96	= 4·8	,,
Paraffins		= 4·0	,,

Graph 10.—Xylene in Commercial Toluole.

4. **Correction for carbon disulphide.**—Carbon disulphide does not appear in toluoles containing more than 60 per cent. of toluene, but it is likely to be present in 50/90's benzoles, and it must be removed before the determination of toluene is

Graph 11.—Benzene in Commercial Toluole.

begun. This is effected by means of alcoholic potassium hydroxide solution, the carbon disulphide being removed as xanthate. The alcohol used must be either pure ethyl alcohol or industrial methylated spirit free from paraffins and pyridine.

The subsequent procedure is described on p. 262. The results obtained by the foregoing method usually fall within 1 per cent. of the true figure for the lower percentages of toluene, and within 0·1 per cent. for the highest.

Claxton and Jones have devised a hitherto unpublished method for the determination of benzene, toluene and xylene in commercial toluole, which method is rather more straightforward than that of Northall-Laurie and has been adopted for *Standard Methods* 1938. The standard distillation apparatus for refined lower boiling products (see p. 223) is used in conjunction with a standard thermometer ranging from 70° to 130° C. One hundred ml. of the sample is distilled by the standard method, the temperature at which 5 ml. has distilled being read as a running-point and the volume of distillate at 120° C. (stop-point) being ascertained. Temperature corrections are of course observed. The percentage of xylene is ascertained from Graph 10 (p. 251) and the result referred to Graph 11 (p. 252), whereby the percentages of benzene is ascertained. Toluene is obtained by difference. Paraffins are determined on a separate portion of the sample and deducted proportionately from the percentages of benzene, toluene and xylene.

Differences in thermometric lag cannot be coped with in Graphs such as numbers 10 and 11, and it is therefore advisable to check the results by examination of mixtures prepared from the pure hydrocarbons.

(e) *The Estimation of Metaxylene in Xylole*

The method of Reichel has been adopted as the Standard Method. The material is treated with nitric acid under controlled conditions and the resulting trinitrometaxylene is crystallized from an acetone solution. Allowance is made for the material remaining in solution.

Exactly 5 ml. of the sample, 20 ml. of glacial acetic acid and 25 ml. of 94/95 per cent. nitric acid are shaken together, in the cold, in a 500 ml. conical flask ; 40 ml. of 98 per cent. sulphuric acid is added with continued shaking and cooling from time to time in ice water. After standing for half an hour at room temperature the flask is heated for one and a half to two hours on a boiling water bath, then cooled in ice water and 450 ml. of cold water added. After standing for half an hour in ice water the crystalline mass which separates is filtered through a glass crucible (Jena 2G3) and washed with small quantities of water (150 ml. in all).

The crystalline solid is sucked as dry as possible and transferred to a weighed 200 ml. conical flask. The flask is fitted with a reflux condenser and the material digested with 100 ml. of acetone for half an hour on a boiling water bath. Crystallization is encouraged by cooling in ice and shaking occasionally, the trinitrometaxylene being

separated by filtering through the same crucible at 15° C. It is dried under specified conditions and the weight of the derivative is obtained. The flask is also dried and weighed, so that the weight of any of the derivative which may have remained adhering to the flask may be ascertained. Under the conditions of the test as fully particularized in *Standard Methods*, the correction for the solubility of trinitrometaxylene in acetone is 0·6 g. The percentage of metaxylene is $(W+0{\cdot}6)\times 100/9{\cdot}8$.

(f) *The Estimation of Xylene in Solvent Naphtha, etc.*

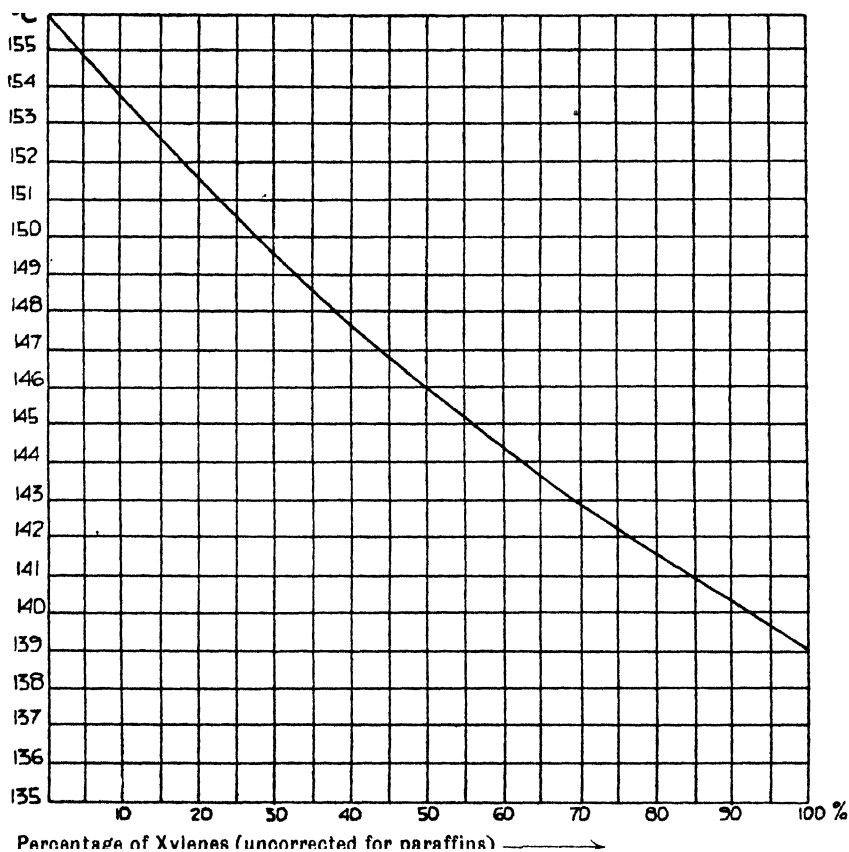
The three isomers of xylene, of differing boiling-point and sp. gr., are present in solvent naphtha along with a complex mixture of cumene, trimethyl benzenes and other substances which boil up to 170° and above. If, however, the benzene, toluene and xylene are removed by careful and repeated fractionation it is found that the solvent naphtha fraction boiling between 143° and 170° from different makes of solvent naphtha has practically a constant boiling-point when examined in a constant boiling-point apparatus. Commercially pure xylole fractionated between 138° and 143° has, under the same conditions, a constant boiling-point of 139·15°. Spielmann and Butler Jones,[1] from an examination of known mixtures of xylole with the 143° to 170° fraction as above, have constructed a boiling-point curve (Graph 12, opposite) from which the composition of unknown mixtures may be inferred from their boiling-point. The Northall-Laurie method for determining boiling-points in the testing for benzene, toluene and xylene in toluole has been combined with the Spielmann and Butler-Jones proposals (*loc. cit.*), resulting in a Standard Method for the determination of xylene in certain mixtures, described in the 1938 edition of *Standard Methods*.

The method was originally devised for the examination of mixtures of xylene with the hydrocarbons which boil between 139° and 170° C., obtained by fractionating washed benzole or washed solvent naphtha between 138° and 170° C. through a 12-bulb pear column. The test is based on the assumption that this fraction behaves as if only two components are present, namely xylene boiling at 139° C. and a hydrocarbon mixture boiling at 156° C. The test is useful in the examination of solvent naphtha but must be used carefully and the results interpreted with due caution.

A standard boiling-point flask based on the Northall-Laurie principle is fitted with a reflux condenser in the auxiliary neck of the flask. A standard thermometer (130° to 160° C.) is fitted with its bulb within the glass cylinder in the main neck of the flask and the bottom of the capillary level with the lower edge of the side-tube

[1] *J. Soc. Chem. Ind.*, 1917, 36, 489.

joint. The flask is supported 83 mm. above the top of a Bunsen burner which is screened from draughts. The flask rests on a sheet of asbestos having a central hole 32 mm. in diameter. A square of cardboard is slipped over the cork carrying the thermometer, to protect the latter from convection currents. The whole apparatus is well screened from draughts.

50 ml. of the sample is heated at such a rate that the condensate runs back at the uniform rate of one drop per second, preferably kept under check by using a metronome. When the temperature becomes

GRAPH 12.—Xylene in Certain Mixtures.

constant it is read and corrected for barometric pressure according to the standard instructions. Reference of the corrected boiling-point to Graph 12 gives the xylenes content uncorrected for paraffins.

The paraffins are determined on the distillate from 138° to 142° C. in the fractionation of a separate portion of the sample through a standard 12-bulb column and the appropriate correction is made, the paraffins being determined by the method described on p. 267. If a

portion of the sample distils below 138° C. in the fractionation, the xylenes in that portion are determined by the method given on p. 257.

The method is sensitive to test conditions and the standard technique as described in *Standard Methods* must be followed in every particular if reliable results are to be obtained.

The following examples are taken from the paper by Spielmann and Butler-Jones (*loc. cit.*) and will show how the results are worked out on the present-day Standard Methods.

Examples:

1. Paraffins and naphthenes absent.

Volume of distillate up to 138° = 22·1 ml. This 22·1 ml., after mixing with 57·5 ml. of pure toluene and 20·4 ml. of pure benzene, gave, on analysis according to (a) (p. 238), benzene, nil; toluene, 6·2 ml.; xylenes, 15·9 ml. (by difference). The volume of distillate from 138° to 170° = 69·7 ml. The boiling-point of this fraction (f) (p. 254) was 143·25° (corrected). Reference to Graph 12 gave for this fraction a content of 67·2 per cent. of xylenes. Total content of xylenes is, therefore,

$$15{\cdot}9+\frac{69{\cdot}7}{100}\times 67{\cdot}2 = 63 \text{ per cent.}$$

2. Paraffins including naphthenes present.

If paraffins including naphthenes are present 100 ml. (or an adequate amount) are distilled through a Young 12-bulb pear column at the rate of 4 ml. per minute and the fraction boiling between 138° (corrected) and 143° (corrected) collected separately. 10 ml. or 20 ml. of this fraction is treated for the determination of paraffins (p. 267). Thus, 100 ml. of original sample gave 23 ml. boiling between 138° and 143° and 20 ml. of this fraction contained 2·5 ml. of paraffins. Correcting the xylene content as determined in example (1) above, $\frac{63}{20}\times 2{\cdot}5 = 8$ per cent. of paraffins associated with xylenes, and the analysis of the sample is then, xylenes $63-8 = 55$ per cent.; associated paraffins including naphthenes = 8 per cent.

(g) *Benzene, Toluene and Xylene in Certain Mixtures*

The methods described under (d) and (e) above, together with the two described below, are all based on the assumption that the mixtures examined contain only benzene, toluene and xylene. They are however applied freely to various acid-washed materials such as 90's benzole, refined toluole, etc., any assumption regarding the distribution of the impurities such as paraffins being quite arbitrary unless confirmed specially and independently.

Eventually, it may be possible to analyse any mixture of benzene, toluene and xylene by one simple distillation, but at present the choice of method for the analysis of a particular sample must depend on the applicability of each test; samples just outside the applicability range of a particular test may be brought within it by the addition of an appropriate amount of one or more pure constituent, allowances being made for this addition in the calculation of the results.

Both the following techniques represent a part of the Colman and Yeoman test described *in extenso* under section (a), p. 238 above, but they have been presented as separate therefrom in the 1938 edition of *Standard Methods* in view of their somewhat frequent application other than as steps in the Colman and Yeoman method of analysis.

(i) *Benzene and toluene* may be determined in mixtures of the two containing between 55 and 97 per cent. of benzene (initially or after the addition of a known amount of either constituent to bring the benzene content within this range) as indicated in the next paragraph; 90's benzole may usefully be examined by this method.

100 ml. of the material is distilled at the rate of 7 ml. per minute, the standard apparatus being used, except that a standard distillation flask of 100 ml. capacity is used. A standard thermometer reading 70° to 130° C. is employed. Normally, the distillate to 85° C. (stop-point) is taken and measured at laboratory temperature, but if the sample contains more than 20 per cent. of toluene, 90° C. is made the stop-point. The toluene content is obtained by referring the volume of distillate at 85° C. (or 90° C.) to Graph 3, p. 240; the benzene content is obtained by difference.

Check tests on known mixtures of the two hydrocarbons should be carried out in view of the variation in thermometric lag between different thermometers. The specified temperatures are of course corrected when necessary for prevailing barometric conditions.

(ii) *Benzene, toluene and xylene* in mixtures containing between 50 and 75 per cent. of toluene and about 14 to 35 per cent. of benzene and a balance of xylene may be examined as indicated below. If the test is applied to samples containing paraffins additionally, it may usually be assumed that the paraffins are distributed proportionately between the benzene, toluene and xylene.

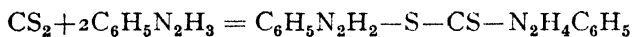
The apparatus is as in (i) above, 100 ml. of sample is again distilled and the distillation rate is the same. Cuts are made at 105° and 116° C. (both stop-points) and the fractions "up to 105° C." and "between 105° and 116° C." are measured at laboratory temperature. The residue in the flask is measured at the same temperature. The sum of the three portions must be at least 99·5 ml.

The volumes of the first and residual fractions are referred to Graph 4, p. 240, to obtain the toluene and benzene contents, the xylene content being obtained by difference. Paraffins, if present, are determined by the method described on p. 267 and the figure deducted proportionately from the figures previously obtained for the benzene, toluene and xylene contents. Temperature corrections for barometric pressure and check tests to eliminate errors arising from thermometric lag characteristics of the thermometer should be applied.

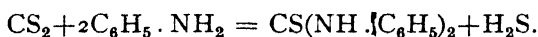
(h) *The Detection and Estimation of Impurities*

Most of the impurities, especially the paraffins, carbon disulphide and thiophen tend to accumulate, on account of their low boiling-points, in the 90's benzole, whilst others such as indene, coumarone, ethyl benzene, etc., are more frequently found in the higher fractions. The following are the chief methods employed for their detection and determination :—

1. *Carbon Disulphide.* This substance may be detected by the phenylhydrazine method of Liebermann and Seyewetz.[1] The method is convenient as it can be carried out without previous treatment of the sample of benzole, but it is of inferior value to other methods. 10 ml. of the benzole to be tested is treated with four or five drops of phenylhydrazine and, after repeated shaking, allowed to stand for fifteen minutes. A crystalline precipitate of phenylhydrazine phenylsulphocarbazide is formed ; the reaction takes place according to the equation :—

$$CS_2+2C_6H_5N_2H_3 = C_6H_5N_2H_2-S-CS-N_2H_4C_6H_5$$

0·2 per cent. of carbon disulphide forms a thick magma of crystals, and when 0·03 per cent. is present the reaction is still quite distinct, the smallest amount detectable being about 0·02 per cent.

According to Bay,[2] the method may be made quantitative, but Spielmann and Butler Jones [3] found that no quantitative results were possible owing to the fact that the solubility of the precipitate is too high to permit washing with benzene. Votoček and Potměšil [4] test for carbon disulphide by Hofmann's reaction, namely, the formation of diphenylthiourea according to the equation :—

$$CS_2+2C_6H_5 . NH_2 = CS(NH . C_6H_5)_2+H_2S.$$

This reaction occurs rapidly in alkaline solutions, and the alkali sulphide which is formed is readily detected by sodium nitroprusside ; the test is quickly carried out, not taking longer than fifteen minutes.

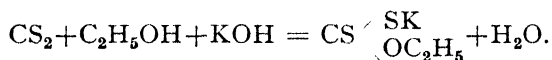
Feigl and Weisselberg [5] state that a characteristic brown to black colloidal suspension of lead sulphide is obtained when a drop of carbon disulphide solution is treated with an alkaline solution of sodium plumbite and formaldehyde. A more sensitive reaction comprises heating the solution to be tested in a closed test-tube, placed in a water bath, a few crystals of nickel acetate and of Hectors' base being added to the solution. A rose colour is produced if 0·0005 mg. of carbon disulphide is present in 1 ml. of the solution tested ; if a red precipitate is formed it may be used for the gravimetric determination of the carbon disulphide. The formation of the rose colour or red precipitate

[1] *Ber.*, 1891, **24**, 789.
[2] *Compt. rend.*, 1908, **146**, 132.
[3] *J. Soc. Chem. Ind.*, 1919, **38**, 185 T.
[4] *Chem.-Ztg. Rep.*, 1901, **25**, 275.
[5] *Z. anal. Chem.*, 1931, **83**, 93.

is due to the production of a complex nickel salt of the empirical formula, $C_{30}H_{22}N_8S_6Ni$.

Methods for the quantitative determination of carbon disulphide in benzole fall into three main classes. The first involves its conversion to and estimation as xanthate; the second, the oxidation of the carbon disulphide and its estimation as sulphate; the third class comprises colorimetric methods.

Frank's method, which depends on Hofmann's [1] reaction and the volumetric determination of the carbon disulphide as insoluble copper xanthate, is characteristic of the first class, and is in general use. The reaction takes place according to the equation :—

$$CS_2+C_2H_5OH+KOH = CS\begin{matrix}\diagup SK \\ \diagdown OC_2H_5\end{matrix}+H_2O.$$

The estimation is carried out as follows: 50 g. of the benzole to be tested is well mixed with 50 g. of alcoholic potassium hydroxide solution (11 g. of potassium hydroxide in 90 g. of absolute alcohol) and allowed to stand for some hours at the ordinary temperature. The whole is then shaken up with about 100 ml. of water, the aqueous layer separated from the benzene, the latter again washed several times with water and the washings added to the aqueous solution containing the xanthate. This solution, or an aliquot portion, is then titrated with a solution containing 12·475 g. of copper sulphate crystals per litre, which corresponds to 0·0076 g. of carbon disulphide per millilitre. For this purpose it is neutralized with acetic acid and the copper solution added until a drop of the solution placed on filter paper next to a drop of potassium ferrocyanide solution forms at the point of contact a reddish brown zone of copper ferrocyanide. The end-point is also plainly indicated by the coagulation of the copper xanthate, which at first is finely divided. The above quantity of alcoholic potassium hydroxide solution is sufficient if less than 5 per cent. of carbon disulphide is present, as in 90 per cent. and 50 per cent. benzoles, which contain on the average from 0·2 to 1·0 per cent., and from 0·0 to 0·5 per cent. respectively. Benzole forerunnings, on the other hand, often contain considerably more than 5 per cent. of carbon disulphide, in which case the quantity of benzole used must be reduced or more alcoholic potash employed. Higher boiling benzoles do not contain carbon disulphide.

According to Spielmann and Butler Jones [2] the potassium ferrocyanide may be used as an internal indicator, the yellow to brownish colour change being as sharp as when external indication is used.

[1] *Ber.*, 1880, **13**, 1732; *cf.* also Nickels, *Chem. News*, 1881, **43**, 148, 250; 1885, **52**, 170; Biehringer, *Dingl. polyt. J.*, 1890, **276**, 78; *J. Gasbeleucht.*, 1890, **33**, 341; Schmitz-Dumont, *Chem.-Ztg.*, 1897, **21**, 487, 510; Frank, *Chem. Ind.*, 1901, **24**, 262.

[2] *Loc. cit.*

Matuszak [1] considers that xanthate methods which involve precipitation with a copper salt [2] require more technique and time than is generally available and favours iodometric titration of the xanthate solution. The latter, first proposed by Delachanal and Mermet,[3] and later examined by Von Halban and Kirsch [4] is described by Matuszak as follows :—The carbon disulphide is removed by fresh alcoholic potash solution, the potash solution acidified with molar acetic acid until just acid to phenolphthalein but alkaline to litmus, starch indicator added, and the solution immediately titrated with 0·006862 N iodine solution. The reaction is $2KX+I_2=2KI+X_2$ where X = the xanthate radical $SC.S.OC_2H_5$. Each mg. of carbon disulphide requires about 2 ml. of iodine solution. Alternatively, the xanthate solution may be added slowly to a sufficiently acid mixture of standard iodate and excess iodine, and the free iodine titrated with thiosulphate.

Callan, Henderson and Strafford [5] state that sodium diethyl dithiocarbamate is a suitable reagent for the determination of small amounts of copper, an intense golden-brown colour developing on addition of a very dilute solution of a copper salt. Hence a reagent containing a copper salt and diethylamine serves as a sensitive means of determining carbon disulphide. The same method is proposed by Tischler.[6] The Chemical Department of the South Metropolitan Gas Company describes a modification of this method for the estimation of small quantities of carbon disulphide in town's gas, and in benzole and other hydrocarbon oils. The colours produced are assessed by the use of a Weston " Photronic " cell.[7]

For the method of the former investigators four solutions are required :—

1. Benzene is freed from carbon disulphide by refluxing with alcoholic potash solution, diluting and washing with water until free from alkali, and separating, drying and distilling.

2. A standard solution of carbon disulphide in benzene:

(*a*) 1 g. of redistilled carbon disulphide is dissolved in and diluted to 100 ml. with purified benzene.

(*b*) 1 ml. of (*a*) is diluted with purified benzene to 100 ml.; 1 ml. = 0·0001 g. of carbon disulphide.

3. Diethylamine solution: 1 ml. of technical diethylamine is diluted to 100 ml. with purified benzene.

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[1] *Ind. Eng. Chem.*, 1932, **4** (*Anal.*), 98.

[2] Calcott, English and Downing, *Eng. Mining J.-Press*, 1924, **118**, 980; Désy, *Proc. Am. Gas Assoc., Tech. Sect.*, 1927, 1440; Grete, *Annalen*, 1878, **190**, 211; Harding and Doran, *J. Amer. Chem. Soc.*, 1907, **29**, 1476; Huff, *J. Amer. Chem. Soc.*, 1926, **48**, 81; Johnson, *ibid.*, 1906, **28**, 1209; Macagno, *Gazzetta*, 1880, **10**, 485; *Chem. News*, 1881, **43**, 138.

[3] *Ann. chim. phys.*, 1877 (5), **12**, 108.

[4] *Z. physikal Chem.*, 1913, **82**, 327.

[5] *J. Soc. Chem. Ind.*, 1932, **51**, 193 T; cf. *Analyst*, 1929, **54**, 650.

[6] *Ind. Eng. Chem.*, 1932, **4** (*Anal.*), p. 146.

[7] *J. Soc. Chem. Ind.*, 1937, **56**, 287 T.

4. Copper acetate solution: 0·03 g. of copper acetate crystals dissolved in 100 ml. of cold industrial alcohol (64° O.P.).

Standard comparison solutions are prepared by transferring 0·25, 0·50, 0·75 and 1 ml. of solution 2 (*b*) to separate narrow Nessler cylinders of 1 cm. dia., and adding 1 ml. of copper acetate solution and 1 ml. of diethylamine solution. The whole is then diluted to 10 ml. with industrial colourless alcohol (64° O.P.). 1 ml. of solution 2 (*b*) is the upper limit which can be used; above this limit the colour is too intense for accurate matching. 1 ml. of the benzole under test is pipetted into a narrow Nessler cylinder, 1 ml. of copper acetate solution and 1 ml. of diethylamine solution added, and the mixture diluted to 10 ml. with alcohol. If the colour is too intense, 1 ml. of the benzole under test is diluted with purified benzene, so that 1 ml. of the diluted sample will contain 0·000025 to 0·0001 g. of carbon disulphide and the test repeated. Finally, for accurate comparison, fresh solutions are prepared, the copper acetate solution being added to the test solution and the standard comparison solutions at the same time. Twenty minutes is allowed to elapse after the addition of the 10 ml. of alcohol before making the comparison. One part of carbon disulphide per million parts of benzene can be detected by this method, and thiophen does not interfere with the reaction. The method is also equally applicable to toluene, xylene, etc.

Another colorimetric method, but one which is not so sensitive, is described by Spausta [1] for the testing of motor benzole; a red coloration develops when ferric chloride in sulphuric acid solution is added to the benzole after treatment with alcoholic potash. An aliquot portion of the benzole under test is shaken for one to two minutes with 3 ml. of normal potassium hydroxide in 96 per cent. alcohol, water then being added to dissolve the potassium salt. A solution of ferric chloride in sulphuric acid gives a red coloration to the benzene in the presence of carbon disulphide, the depth of which is matched against solutions of known carbon disulphide concentration. The test is sensitive to 0·05 per cent. of carbon disulphide in the solution.

Stavorinus [2] oxidizes the potassium xanthate to sulphate with hydrogen peroxide solution. The excess of alkali is determined by titrating the resulting solution with standard sulphuric acid. Hoffert, Claxton and Hancock [3] apply a modification of this method to crude and refined benzoles. 30 g. of caustic soda is dissolved in 20 ml. of water and the resulting solution is added to 500 ml. of absolute alcohol. Any potassium carbonate separating out on standing for twenty-four hours is filtered off through glass wool. 20 ml. of the benzole is added to 10 ml. of this solution in a dry 200 ml. conical flask and well mixed. The alcohol and the greater part of the benzole are then evaporated off on a water-bath after which 30 ml. of distilled water and 2 ml. of a 30 per cent. solution of hydrogen peroxide (100 vols.) are added. After well mixing, heating is continued for fifteen to twenty minutes to

[1] *Petroleum*, 1930, **26**, 7.
[2] *J. Gasbeleucht.*, 1906, **49**, 8; *Chem. Zentr.*, 1916, **1**, 706.
[3] *J. Soc. Chem. Ind.*, 1935, **54**, 245 T.

decompose the excess hydrogen peroxide. The solution is cooled, 6 to 10 drops of bromophenol-blue indicator (0·04 per cent.) added and then titration carried out with 0·5 *N.* sulphuric acid, further indicator being added if required. A blank determination must be made at the same time, omitting the benzole. If the corrected number of ml. of 0·5 *N.* acid is T—A, the percentage of sulphur as carbon disulphide is calculated from 0·0401 (T—A)/S, where S is the sp. gr. of the benzole at the temperature of the test. If the benzole contains more than 0·8 per cent. of sulphur as carbon disulphide it should be suitably diluted with benzene free from carbon disulphide, or a correspondingly smaller amount of benzole should be used initially. The concentration of the alcoholic potash solution alters on keeping and a blank determination must always be made at the time of the test. The distilled water must be neutral to bromophenol-blue. Hydrogen sulphide, sulphur dioxide, mercaptans and pyridine bases interfere with the determination and must be removed from the benzole before testing. Gravimetric methods, involving the precipitation of copper xanthate with excess copper sulphate solution, and the ignition of the precipitate to copper oxide,[1] are stated by Spielmann and Butler Jones[2] to give variable results. Higgins and Pollard[3] review methods available for the determination of small concentrations of carbon disulphide in air.

The British Standard *qualitative test* for carbon disulphide consists in shaking 5 ml. of the sample with 1 ml. of freshly distilled phenylhydrazine in a 10 ml. stoppered cylinder when, if carbon disulphide is present, a white precipitate is formed. The test may be made *roughly* quantitative, as the amount of precipitate is approximately proportionate to the carbon disulphide content, but the standard quantitative method described below must be used where reasonable accuracy is required.

The *quantitative test* presented as the Standard Method is based on the formation of xanthate and titration of the extracted xanthate with iodine solution after acidification. Hydrogen sulphide and sulphur dioxide affect the results, and anything more than a trace of either must first be removed by washing with caustic soda solution; mercaptans also affect the test and, if present, must be removed by shaking with silver nitrate solution. These treatments must be followed by a water wash.

As reagents, approximately *N.* alcoholic caustic potash solution, 0·1 *N.* iodine solution and freshly prepared starch solution are required.

20 ml. of the sample (washed for hydrogen sulphide, sulphur dioxide and mercaptans as above if required) is mixed with about

[1] *Cf.* Johnson, *J. Amer. Chem. Soc.*, 1906, **28**, 1209.
[2] *J. Soc. Chem. Ind.*, 1919, **38**, 185 T.
[3] *J. Soc. Chem. Ind.*, 1937, **56**, 122 T.

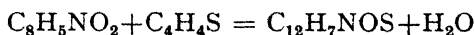
10 ml. of the alcoholic potash solution in a short-stemmed separating funnel. The (homogeneous) mixture is allowed to stand at least five minutes and then extracted three times with water. The combined extracts are acidified with about 7 ml. of roughly 2 *N*. acetic acid and titrated with the iodine solution, using the starch solution as indicator in the usual way. The sulphur present as carbon disulphide is $0{\cdot}64\ v/V\rho$, where V and v are the volumes of sample and 0·1 *N*. iodine respectively and ρ is the density of the sample at the test temperature.

The quantities of sample, alcoholic potash and water for extraction are adjusted according to the amount of carbon disulphide present. *Standard Methods* gives details of the amounts for varying ranges of carbon disulphide contents.

The foregoing quantitative test is used in British standard practice when the carbon disulphide content is required separately. When only a reasonably approximate figure is required, especially in the comprehensive analyses represented by such tests as that of Colman and Yeoman, where the figure is mainly of interest as a correction figure for the contents of the major constituents of the sample, a method based on the difference in sp. gr. before and after removal of the carbon disulphide is recognized. A description of the principles of this method appears on p. 244 in connection with the second part of the Colman and Yeoman test.

2. *Thiophen.* Aniline prepared from benzene containing thiophen resinifies much more readily than aniline prepared from thiophen-free benzene: the yield of resorcinol is much diminished unless only very little thiophen is present; much more resin is formed in aluminium chloride condensations if thiophen is present, and thiophen acts as an inhibitor in certain other catalytic reactions.

A characteristic reaction for the detection of thiophen in benzene is the coloration produced by isatin and sulphuric acid. In the case of thiophen this is a beautiful blue ("indo-phenine"); in the case of thiotolen it is blue with a reddish tinge, and with thioxene reddish violet. The reaction [1]:

$$C_8H_5NO_2+C_4H_4S = C_{12}H_7NOS+H_2O$$

is carried out as follows :—

Several millilitres of pure sulphuric acid are poured over a few pieces of isatin placed in a shallow porcelain dish which has been rinsed out previously with pure sulphuric acid. A layer of benzole is then poured over the acid, the dish covered with a watch-glass and allowed to stand. If the benzole is pure, no blue rings will form round the isatin within an hour. Further particulars of this test are given by Bauer,[2] Storch,[3] and Liebermann and Pleus.[4] Liebermann [5] recommends nitroso-

[1] Victor Meyer, *Ber.*, 1882, **15**, 2893; Baeyer and Lazarus, *ibid.*, 1885, **18**, 2637.

[2] *Ber.*, 1904, **37**, 1244, 3128.

[3] *Ibid.*, 1904, **37**, 1961.

[4] *Ibid.*, 1904, **37**, 2461.

[5] *Ibid.*, 1887, **20**, 3231.

sulphuric acid or amylnitrite and sulphuric acid as a sensitive reagent for thiophen. Wray,[1] in accord with Bauer,[2] states that the indophenine coloration does not take place when pure sulphuric acid is used, a green solution being obtained which, however, turns blue on the addition of oxidizing agents, such as nitric acid or ferric chloride. Accordingly, in testing commercial benzoles, it is advisable in all cases to add an oxidizing agent, preferably a drop of nitric acid. To test a benzole for thiophen, 25 ml. of a solution of 0·5 g. of isatin in 1000 g. of pure sulphuric acid is placed in a stoppered cylinder of 100 ml. capacity, and 1 ml. of the benzole to be tested is added, followed by 25 ml. of pure sulphuric acid containing one drop of nitric acid. The cylinder is then closed and the whole well shaken, when the blue indophenine coloration is immediately obtained.

The Standard Method for the *qualitative* test for thiophen is based on the isatin reaction; 1 ml. of the sample is added to 25 ml. of 0·05 per cent. isatin in sulphuric acid; 25 ml. of pure sulphuric acid containing one drop of concentrated nitric acid is added and the whole mixed. The absence of unsaturated hydrocarbons must be checked as the test is inapplicable in the presence of these bodies; the check may be made by shaking 2 ml. of the sample with a mixture of 10 ml. of *N.* sulphuric acid and 1 ml. of 0·5 *N.* bromide-bromate solution. If the colour is discharged, unsaturated hydrocarbons are indicated; they may not be removed by acid washing and the isatin test then applied, as such washing inevitably results in the removal of some at least of the thiophen. There is no known reliable method for the detection of thiophen in the presence of unsaturated hydrocarbons.

The addition of nitric acid may be employed with advantage for the colorimetric method as described by Schwalbe.[3] The latter investigator regards methods of estimating thiophen by means of mercury compounds (see p. 265) as inaccurate, stating that even thiophen-free benzene gives precipitates with mercury salts. He studied the qualitative indophenine reaction and worked it out as a quantitative method. Differences of 0·02 per cent. of thiophen can be easily recognized, 0·05 per cent. being the minimum and 0·5 per cent. the maximum quantity for which the method is available.

To carry out the test a number of standard solutions are prepared from benzene, free from thiophen, and from absolutely pure thiophen, of the following concentrations:—0·5, 0·25, 0·1, 0·075, 0·05, 0·025 and 0·01 per cent. A solution of 0·5 g. of isatin in 1000 g. of pure concentrated sulphuric acid is also prepared; this solution will keep for months. Two portions, each of 25 ml. of the isatin sulphuric acid reagent are introduced into two 100 ml. flasks, 25 ml. of pure concentrated sulphuric acid added to each, and then to one of them 1 ml. of the benzene-thiophen test solution and to the other 1 ml. of the benzene to be tested. The flasks are stoppered, shaken well for five minutes, allowed to settle, and the resulting colorations compared against a white background. The smaller the content of thiophen, the more gradual is the appearance of the coloration and the more green the shade of colour. An interval of fifteen minutes is sufficient for the comparison of the results. If a commercial benzole is to be tested, a commencement is made with the 0·5 per cent. test solution, and then with the more dilute test solutions in turn. In the case of pure benzenes it is sufficient to test downwards from 0·25 per cent. or from 0·1 per cent.

The test, if carried out in a stoppered flask as described above, gives absolutely no recognizable green coloration when the thiophen content is 0·025 per cent., but only a faint grey discoloration of the yellow solution of the isatin reagent. If, however, the reaction is carried out in a porcelain basin, a green coloration, soon

[1] *J. Soc. Chem. Ind.*, 1919, **38**, 83 T.
[2] *Loc. cit.*
[3] *Chem.-Ztg.*, 1905, **29**, 895.

followed by blue, is obtained without difficulty with this proportion of thiophen. By employing a basin and comparing with test solutions of 0·025 and 0·01 per cent. of thiophen, very low concentrations of thiophen can be estimated.

Gravimetric methods of estimating thiophen have been suggested in which a precipitate is obtained with either basic mercuric sulphate or acetate[1]; a variant of such a method dependent upon the rate of formation of the basic mercuric sulphate—thiophen precipitate[2] and a further modification employing a volumetric method.[3] Dimroth[4] claimed to have prepared the compound $C_4H_2S(Hg . OH)(Hg . O . CO . CH_3)$ as a white insoluble powder, but Schwalbe[5] suggested that the substance was a mixture. Paolini[6] states that the substance prepared by the reaction between thiophen and mercuric acetate has the composition, $C_4H_4S(Hg . O . CO . CH_3)_4$. Briscoe, Peel and Young[7] state that the product formed by shaking thiophen with a saturated solution of mercuric acetate is diacetoxymercurithiophen, $C_4H_2S(Hg . O . CO . CH_3)_2$, a white insoluble powder produced by a reaction similar to that shown by Volhard[8] to occur between thiophen and mercuric chloride. The product of the interaction of thiophen with basic mercuric sulphate is described by these investigators as dihydroxymercurithiophen mercurisulphate, $C_4H_2S(Hg . OH)_2, HgSO_4$, a white insoluble powder identical in composition with the substance obtained by Spielmann and Schotz.[9] These mercury derivatives are insoluble powders, decomposing when heated and only partially decomposed on boiling with concentrated hydrochloric acid; in sulphuric acid solution they give the indophenine colour reaction.[9] Spielmann and Schotz[10] have examined the various methods and find that the accuracy of the results is dependent on the proportions of the reacting substances, the temperature of their preparation and precipitation, time, and the amount of shaking.

The modified basic mercuric sulphate method recommended by Spielmann and Schotz is the Standard Method.

A glass-stoppered test-tube and either a Gooch crucible (prepared with acid-treated asbestos and fitted with a perforated plate on the asbestos) or a 2G3 glass filtering crucible are required. Whichever crucible is used, it is dried at 100°/115° C., cooled and weighed before use. The reagent is made by adding first 100 ml. of distilled water and then 20 ml. of concentrated sulphuric acid, with vigorous stirring, to about 5 g. of mercuric oxide in a porcelain basin. The (colourless) solution is filtered and stored in a glass-stoppered bottle.

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[1] Dimroth, *Ber*, 1899, **32**, 758; Paolini and Silbermann, *Gazzetta*, 1915, **45** (ii), 388; Denigès, *Compt. rend.*, 1895, **120**, 628, 781, 963; 1908, **126**, 1868; *Bull. Soc. chim.*, 1898, **19**, 754; *Analyst*, 1895, **20**, 188.

[2] Denigès, *Bull. Soc. chim.*, 1895, **13** (3), 537.

[3] Denigès, *ibid.*, 1896, **15** [3], 862, 1064; *Analyst*, 1896, **21**, 297, 303.

[4] *Loc. cit.* [5] *Ber.* 1905, **38**, 2208. [6] *Gazz. Chim. Ital.*, 1907, **37** (i), 58.

[7] *J. Chem. Soc.*, 1929, 2589. [8] *Annalen*, 1892, **267**, 172.

[9] *J. Soc. Chem. Ind.*, 1919, **38**, 188 T. [10] *Loc. cit.*

About 20 ml. of reagent is measured into the stoppered tube, followed by 2 ml. of sample from a burette. The tube is closed and shaken vigorously for three hours in a shaking machine. Filtering off and washing of the precipitate follow, the washing continuing until the filtrate is neutral to litmus. The crucible and contents are dried at 110°/115° C. and weighed.

Quantitatively, the precipitate is represented by the formula $(HgO, HgSO_4)_2C_4H_4S$,[1] and the sulphur present as thiophen in the sample is therefore $0{\cdot}029 \times 100W/2\rho$ where W is the weight of precipitate and ρ the density of the sample at the temperature of test. Carried out in strict accordance with the requirements of *Standard Methods*, it is claimed that the results fall within $\pm 0{\cdot}005$ of the true value.

The test is limited to samples free from unsaturated hydrocarbons. As in the thiophen test, the sample may not be washed with acid to remove unsaturateds and then subjected to the quantitative test, as acid washing removes some at least of any thiophen present.

Under the above experimental conditions, Spielmann and Schotz state that only thiophen reacts, any carbon disulphide present, which is most likely to interfere with the formation of a precipitate from thiophen and basic mercuric sulphate alone, taking no part in the reaction.[2]

On the whole the above mercuric sulphate method is to be preferred, since the reagent used is stable, side reactions are notably absent, previous practice is not essential to success, and a high degree of accuracy is attainable. The basic mercuric acetate method, as modified by Spielmann and Schotz,[3] may, however, be relied upon to give satisfactory results. If Paolini and Silbermann's reagent is used, the precipitate formed is stated to have a composition agreeing with the formula $SC_4(HgC_2H_3O_2)_4$. For details of the method of carrying out the test, the original paper should be consulted. The estimation of thiophen in pure benzole, along with other impurities, is described on p. 248.

3. *Thiotolen* (α-thiotolen, b.p. 112° to 113° ; β-thiotolen, b.p. 114° (corr.)). α- and β-thiotolen have been identified in coal tar by oxidation of coal-tar thiotolen and the production of α and β thiophenic acids.[4] A simple method of obtaining thiotolen is to dilute the sulphuric acid employed to wash the toluene with 20 per cent. of water, and to pass steam in slowly at 100°. Thiotolen, being more easily decomposed than thioxene, comes over and is fractionated.[5] The detection of thiotolen by the well-known Laubenheimer test[6] is carried out according to Spielmann,[7] as follows :—

3 ml. of a concentrated solution of phenanthraquinone in glacial acetic acid is introduced into a cylinder containing 10 ml. of the

[1] *Cf.* Briscoe, Peel and Young, *loc. cit.*

[2] *Cf.* Denigès, *Bull. Soc. chim.*, 1915, 17 (4), 353; Schwalbe, *Z. Farben- und Textil-Ind.*, 1915, 4, 113.

[3] *Loc. cit.*

[4] Gattermann, Kaiser, and Meyer, *Ber.*, 1885, 18, 3005.

[5] Schulze, *Ber.*, 1884, 17, 2852.

[6] *Ber.*, 1875, 8, 224.

[7] *Constituents of Coal Tar*, London, 1924, p. 151.

toluole to be tested. 1·5 ml. of concentrated sulphuric acid is then added, and the vessel shaken cautiously under a stream of water. The probable presence of thiotolen is shown by a green colour. Confirmation is obtained as follows :—

3·5 ml. of water is added cautiously with continuous cooling. The upper layer is removed by means of a pipette, and the lower layer gently agitated with one or more volumes of ether which, if thiotolen is present, assumes a bluish wine-red colour. This colour, which is the usual one, is evidently that of the mixed isomerides, as α-thiotolen gives a purple colour, and the β-isomeride a blue colour. It is important that at no stage should there occur an appreciable rise in temperature.

4. *Paraffin Hydrocarbons* (*and Naphthenes*). The paraffins are determined by converting the benzene hydrocarbons into soluble sulphonic acids. All substances which are neither destroyed nor sulphonated by fuming sulphuric acid remain in the residue, which therefore also includes the naphthenes and carbon disulphide ; the latter is determined by one of the methods described on p. 258, and its amount deducted. Benzene and toluene can be sulphonated readily by treatment with several times their volume of 98 to 100 per cent. sulphuric acid ; the concentration should be as near 100 per cent. as possible. The xylenes require fuming sulphuric acid containing 20 per cent. of free sulphur trioxide. Unrefined solvents and naphthas give viscous and solid products with sulphuric acid, so that a special procedure must be adopted (*vide infra*). The Barrett Company of America estimate paraffins including naphthenes by a method which is substantially that of Kraemer and Spilker,[1] except that the treated sample is finally centrifuged in order to effect a clean separation.

According to Kraemer and Spilker this estimation is carried out as follows : 200 g. of the sample is treated in a capacious separating funnel with 500 g. of fuming sulphuric acid containing 20 per cent. of anhydride, and shaken for a quarter of an hour, avoiding undue heating ; the whole is then allowed to stand for two hours. The layer of sulphuric acid is drawn off and the operation repeated twice with the same quantities of fuming acid. After treatment with 1500 g. of acid as above, everything except the paraffins, carbon disulphide, and naphthenes has usually dissolved. The oil remaining in the funnel is collected, and the whole of the acid used is poured, with shaking, upon an equal weight of chopped ice contained in a 3-litre flask, taking care that the temperature does not rise above 40°. The solution is then boiled over a naked flame, and the free hydrocarbons present are distilled off and collected in a 100-ml. separating

[1] Muspratt, *Handbuch der technischen Chemie*, 4th edn., **8**, 43.

funnel, the distillation being continued until 50 ml. of water has passed over after the oil. In this manner all the oil dissolved by the sulphonic acids or mechanically mixed with the liquid is recovered and, after the water has been drawn off, is added to the main quantity. The whole of the oil is then again repeatedly shaken with 30 g. of fuming sulphuric acid containing 20 per cent. of anhydride, until no further reduction in volume takes place, after which it is finally washed with a small quantity of water. The weight of oil obtained, divided by 2, gives the percentage of paraffins in the sample.

According to Hoffert and Claxton [1] none of the many published methods for the determination of paraffins in benzoles is entirely free from objection. The Standard Method (1938) is based on a technique reported by these authors as giving consistent and fairly accurate results. The provisions of the 1938 standard are outlined below :—

80 ml. of sulphuric acid (containing $99 \pm 0{\cdot}5$ parts per 100 by weight of H_2SO_4, checked by titration) is poured into a specially designed and standardized sulphonation unit, and 20 ml. of the sample is accurately measured into the unit. The stopper is inserted, the apparatus inverted and the contents shaken vigorously for ten minutes. During this process, the tap of the unit is kept open and the rise in temperature is checked by cooling. The tap is closed and the unit brought to an upright position. The volume of unsulphonated hydrocarbons is read after settlement and the shaking and separating process is repeated until a substantially constant figure is obtained. The final settlement period is of twelve hours' duration.

Standard Methods provides an alternative form of the sulphonation unit for use when less than 10 per cent. of non-sulphonable hydrocarbons (paraffins and naphthenes) are present ; provision is also made for pre-treatment of the sample if direct sulphonation would result in the formation of viscous or solid products.

Carbon disulphide is determined separately if required, and an allowance made. The unsulphonated hydrocarbons should in any case be tested for the complete removal of aromatic hydrocarbons, by means of the formolite reaction. For this purpose, about 1 ml. of the unsulphonated material is placed in a test-tube with about the same amount of concentrated sulphuric acid and a few drops of 40 per cent. formaldehyde. The mixture is shaken ; a dark red precipitate indicates the presence of aromatic hydrocarbons, but the test is very sensitive and a mere coloration may be ignored. In the event of a positive result, the sulphonation test must be repeated on a fresh portion of the sample.

The quantity of paraffins is scarcely more than 1 per cent. in the

[1] *Motor Benzole, Its Production and Use*, London, 1931, p. 596.

case of the 90's, 50's and 0's benzoles ; toluole usually contains none ; xylole, on the contrary, often contains up to 3 per cent. of paraffins.

An approximate estimation of the naphthene content of a light oil may be obtained by a modification of the method involving the determination of the critical solution temperature of the spirit in freshly distilled pure aniline.[1] A more accurate method is described by Manning and Shepherd.[2]

5. *Free and Total Sulphur.* (a) *Free Sulphur.* In addition to organically-combined sulphur in the form of thiophen, and carbon disulphide, sulphur may be present in benzoles as—

(i) Sulphuretted hydrogen, either as a natural impurity or produced, along with sulphur dioxide, on distillation of a sulphonic-acid contaminated product;
(ii) as free sulphuric acid, and as sulphonic acids due to incomplete refining ; and
(iii) as elementary sulphur resulting from incorrect treatment with sulphuric acid.

With the possible exception of the heavy coal-tar naphthas, freedom from acids, alkalis and sulphuretted hydrogen is customarily specified.

To test for the former, specifications usually prescribe a definite indicator and the neutrality or otherwise is determined by the *Standard Method* as follows :—

10 ml. of distilled water (the preparation of which is prescribed so that the water will be free from contaminating materials from the atmosphere) is taken in a stoppered cylinder with a specified quantity of the indicator required ; 50 ml. of the sample is added and the contents of the cylinder shaken thoroughly. After settlement the colour of the aqueous layer is compared with the contents of a similar cylinder prepared with the indicator but without the sample. The report must specify the indicator used.

Standard Methods requires the cylinders to be of glass which is inert to their contents under the conditions of the test, and also gives the methods of preparing the more usually prescribed indicators.

Hydrogen sulphide is tested for qualitatively in parallel with the qualitative test for mercaptans. As the British standard specifications (both of the National Benzole Association and the British Standards Institution) are based, in respect of hydrogen sulphide, only on the qualitative test, that alone appears in the 1929 edition of *Standard Methods*. The method in outline is described below :—

10 ml. of the sample and 5 ml. of sodium plumbite solution prepared in the prescribed manner are shaken vigorously together in a glass-stoppered cylinder, 50 ml. in capacity and 25 mm. in diameter. Opalescence, followed by darkening, indicates the presence of both

[1] Ormandy and Craven, *J. Inst. Petroleum Tech.*, 1924, **10**, 101 ; *Standard Methods of Testing Petroleum and its Products*, London, 1924.

[2] *Fuel Research Board*, Technical Paper, No. 28, 1930.

mercaptans and elementary sulphur. An immediate black precipitate indicates hydrogen sulphide.

For convenience it may here be indicated that the Standard Method proceeds from this stage to the separate identification of any mercaptans, by the addition of between 0·05 and 0·1 g. of dry flowers of sulphur. The cylinder is shaken for fifteen seconds and allowed to settle for one minute. If the sample and sodium plumbite solution show no change in colour and the sulphur film retains its bright yellow colour the test is reported as negative; if either liquid should be discoloured or the colour of the sulphur masked, the test is reported as positive; if there is only slight discoloration the test is reported as slightly positive.

Various precautionary measures must be taken to ensure that the effect of peroxides (due to oxidation of the sample) and carbon disulphide, and (where inhibitors are suspected) phenolic compounds, do not interfere with the test.

It may also be noted that the test can be applied for mercaptans only by first washing the sample with acidified cadmium chloride, whereby the hydrogen sulphide is removed. The sample is then washed with water before being subjected to the test. Free sulphur is the most harmful of the sulphur impurities in a motor benzole, because of its corrosive nature. The absence of a dark-coloured precipitate when a quantity of benzole is shaken with clean mercury is a qualitative test of freedom from elementary sulphur, but an actual estimation of free sulphur is essential to state that a sample of benzole is free from this impurity. The presence or absence of other impurities, however, also determines the corrosiveness of a benzole, and a simple test of the corrosive tendency of a sample is the copper-strip test.[1]

The Standard Method for the copper strip test is as follows: A piece of electrolytic copper foil is thoroughly cleaned and highly polished by first rubbing with cork moistened with distilled water and dipped in the finest grade emery powder; the foil is then wiped with filter paper moistened with pure acetone. The foil is cut into two strips; one is placed in a clean test-tube and the tube corked, the other being put into a thick-walled test-tube containing 50 ml. of the sample. The latter tube is fitted with a reflux condenser and maintained within two degrees of 50° C. for two hours. The strips are then compared and the result reported under one or other of the following descriptions:—

(1) No change
(2) Slight discoloration
(3) Brown or peacock shade
(4) Steel grey
(5) Black, not scaled
(6) Black scale

[1] Sanders, *J. Chem. Soc.*, 1912, **101**, 358; Lomax, *J. Inst. Petroleum Tech.*, 1917-18, **4**, 6; Hoffert and Claxton, *Report Joint Benzole Res. Comm.*, 1925, pp. 19, 27.

Both free sulphur and hydrogen sulphide are responsible for any discoloration of the copper, but their effect will be influenced by various other substances which may be present, notably peroxides.

The limits of discoloration which are permitted in the British specifications are indicated in the table facing p. 210.

A more stringent test is specified by the Barrett Company (U.S.A.).[1] The copper strip ($2\frac{1}{2}$ by $\frac{1}{4}$ in.), after polishing, is immersed in 200 ml. of the dry benzole contained in a 300 ml. Pyrex flat-bottomed flask, and fitted with a reflux condenser. The flask and contents are then heated for thirty minutes on a gently boiling water-bath; thereafter the strip is immediately withdrawn and examined. According to this Company's specification for standard motor benzole, the copper may show an iridescent or peacock discoloration, but *not* a grey or black deposit or coloration. 0·25 mg. of sulphur per 100 ml. of benzole will cause peacock stains, and 1·0 mg. will cause actual scaling of the copper; the inhibiting effect of various impurities is less at the refluxing temperature.[2]

The method for the determination of free sulphur, originally proposed by Ormandy and Craven,[3] modified by Hoffert and Claxton [4] and standardized in the 1929 edition of *Standard Methods* is not extensively used in the testing of benzoles, etc., in the United Kingdom and is not required by the current British specifications. Hence, it does not appear in the 1938 edition, but particulars are given below as it is a method which is useful on occasion.

The assembled apparatus is shown in Fig. 43. The 250 ml. round-bottomed flask, A, is fitted with a ground-in glass head which possesses an outlet tube and a dropping funnel, the stem of which reaches nearly to the bottom of the flask; the dropping funnel is provided with a stop-cock. B is a wash-flask fitted with delivery and exit tubes inserted through a rubber stopper; C, a flask of about 600 ml. capacity provided with a well-fitting glass stopper which later replaces a rubber stopper carrying delivery and exit tubes; and D, a second wash-flask. The sample is examined for sulphuretted hydrogen which, if present, must be removed by washing thoroughly with 5 per cent. aqueous sodium hydroxide solution. The resulting solution is used for the quantitative determination of the sulphuretted hydrogen, using the above apparatus and the same method of estimation, employing ammoniacal cadmium acetate solution.

[1] The Barrett Company, *Manufacturing Specifications for Coke-Oven Light-Oil Distillates*, 1929.

[2] Hoffert and Claxton, *Motor Benzole, Its Production and Use*, London, 1st edn., 1931; *cf. ibid.*, 2nd edn., 1938, p. 805.

[3] *J. Inst. Petroleum Tech.*, 1923, **9**, 133.

[4] *Report Joint Benzole Res. Comm.*, 1925, p. 30; *Gas. J.*, 1925, **170**, 654.

The sample, freed from sulphuretted hydrogen, is washed with water and dried over anhydrous calcium chloride. 100 ml. of the dried
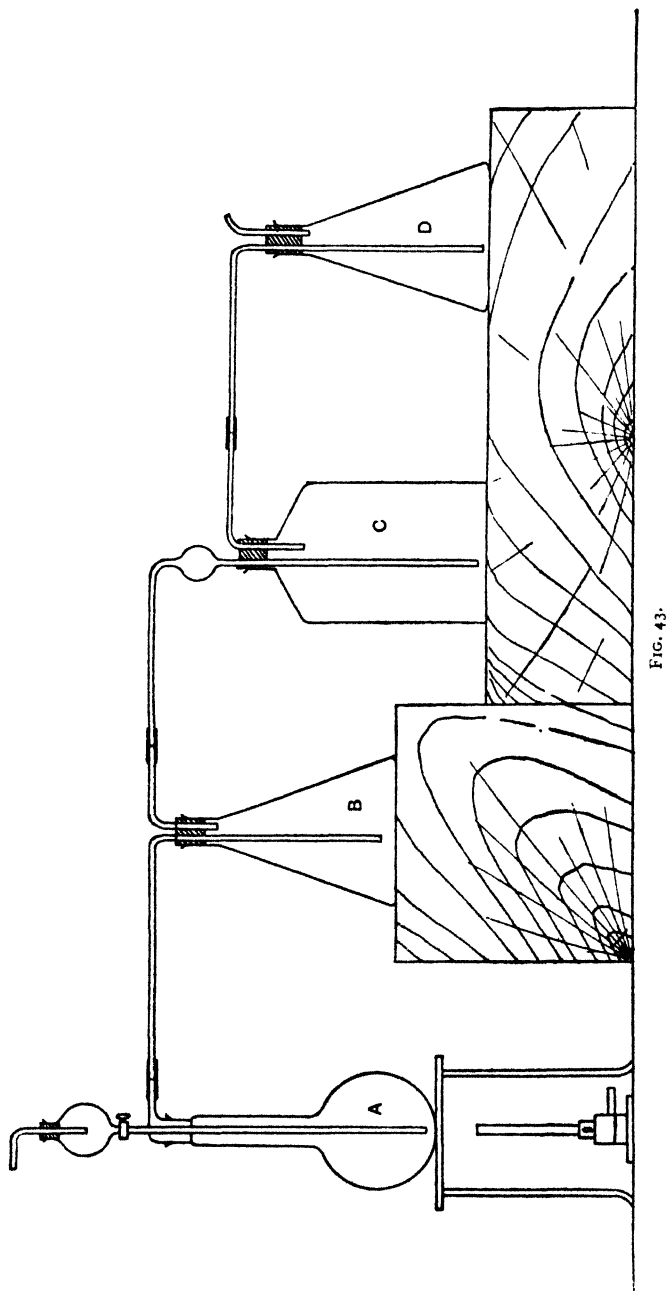
Fig. 43.

spirit is measured into the dry flask A, 2 to 3 ml. of clean mercury added, the flask corked and shaken vigorously until, on standing,

the mercury separates from the sludge which appears if free sulphur is present. The spirit is decanted through a filter paper which is then drained and introduced into the flask A. About 50 ml. of *boiling* distilled water is now placed in the first wash-bottle B; about 50 ml. of ammoniacal cadmium acetate solution is placed in bottle C, and about 25 ml. of the same solution in the last wash-flask D. The ammoniacal cadmium acetate solution is prepared by dissolving 25 g. of cadmium acetate in 200 ml. of 0·880 ammonium hydroxide solution and making up to 1 litre with distilled water. The apparatus is now assembled as shown in Fig. 43, the glass connecting tubes meeting, or being fitted one inside the other; in no circumstances must the hydrochloric acid vapours come into contact with the rubber and the apparatus must be free from leaks.

The apparatus is purged with hydrogen for about ten minutes, the hydrogen being admitted through the funnel, after which the tap of the funnel is closed. 50 ml. of concentrated hydrochloric acid is now placed in the funnel and run into the flask rapidly, except that the last 2 or 3 ml. of acid is retained to seal the tap when closed. The contents of flask A are then boiled for fifteen minutes. Cadmium sulphide should not appear in the last wash-flask. The flasks are finally allowed to cool whilst a stream of hydrogen is swept through the apparatus. The contents of bottle C are now filtered, and, after allowing to drain, the filter paper and its contents are introduced into bottle C with 20 ml. of $N/10$ iodine solution, followed by 5 ml. of concentrated hydrochloric acid. The glass stopper is immediately inserted and the bottle shaken. Any sulphide adhering to the delivery tube is removed by dipping it into the resulting solution and washing down with distilled water. The contents of the bottle are finally diluted to 300 to 400 ml. with distilled water, and titrated with $N/10$ sodium thiosulphate solution, using starch solution as indicator. The weight of free sulphur per 100 ml. of the sample $= 1{\cdot}6 \times (20 - x)$ mg., where x is the ml. of $N/10$ sodium thiosulphate solution required. The reagents should be tested for sulphur by means of a blank experiment and a suitable correction applied.

In addition to the Standard Method for the copper-strip test (p. 270), *Standard Methods* recognizes the Garner and Evans method [1] for the determination of corrosive sulphur; this is a gravimetric test based on refluxing the sample with copper-bronze powder, oxidizing the resulting sulphide to sulphate and precipitating as barium sulphate.

The method is carried out in an atmosphere free from sulphur compounds; 0·5 g. of copper-bronze powder is placed in a flask with 100 ml. of the sample. Boiling under reflux follows for an hour, the flask being shaken round occasionally during this period. The sample

[1] *J. Inst. Petroleum Tech.*, 1931, 17, 451.

is decanted through filter paper, and the washings from treatment of the copper-bronze with 50 ml. of solvent such as petroleum spirit or pure benzole (sulphur-freed by boiling with copper-bronze powder) is also decanted through the filter paper. The flask containing the bulk of the copper-bronze and also the filter paper are dried for a few minutes in a steam oven and 50 ml. of distilled water and an excess of bromine are added to the copper-bronze in the flask. The solution is acidified, the contents of the flask washed into a beaker and the excess of bromine boiled off; the filter paper is similarly treated with bromine in a separate beaker and the liquids combined and, after filtration, reduced to about 75 ml. in bulk by boiling.

The remainder of the method consists substantially in the precipitation of the sulphate with barium chloride, filtration, washing, ignition and weighing in the manner usual for such determinations. A blank is carried in order to determine the allowance for sulphur traces in the materials other than the sample.

(b) *Total Sulphur* in a benzole may be determined either by means of a bomb calorimeter or by burning the benzole (generally after dilution with alcohol) in a suitable lamp apparatus. The former is considered the more accurate method, errors arising in the lamp method due to the small quantity of benzole used, incomplete oxidation of the sulphur compounds and loss owing to the rapid volatilization of the carbon disulphide. The lamp method is, however, in common use and is applied in the Standard Method, due to Davidson,[1] with modifications proposed by Claxton, Hancock and Hoffert.[2] The method is briefly as follows:—

The sample is diluted with alcohol and a known quantity burnt in a lamp, the products of combustion being drawn through neutral hydrogen peroxide solution. The resulting acidity is determined with sodium carbonate solution.

The apparatus is shown in Fig. 44 and *Standard Methods* fully describes the principles of its operation and the details of its construction. The hydrogen peroxide solution is prepared in a prescribed manner and brought to neutrality as defined by the intermediate grey shade of bromophenol blue indicator. A portion of the neutralized solution is used to fill the lute round the inlet tube of the wash-flask and about 100 ml. is poured down the scrubber into the flask. The parts of the burner are cleaned by igniting in a blow-pipe flame, and the burette rinsed and then filled with a stock solution prepared by accurately diluting the sample, in the proportion of 1 : 5, with blending methanol or ethyl alcohol. The top of the burette is closed with a cork, the tap opened to the outlet to secure equilibrium and when stability is attained, the tap is turned to connect the burette with the

[1] *Gas J.*, 1929, **185**, 95. [2] *Gas. J.*, 1932, **199**, 94.

burner. The side tube to the jet in the burette is then opened and the solution flows into the burner to a height governed by the height of the jet. The burner parts are assembled, the lamp lit and the size of the flame adjusted by altering the height of the silica sleeve.

The lamp is allowed to burn in the open until bubbles rise regularly from the jet. The suction on the wash-flask is started and the chimney
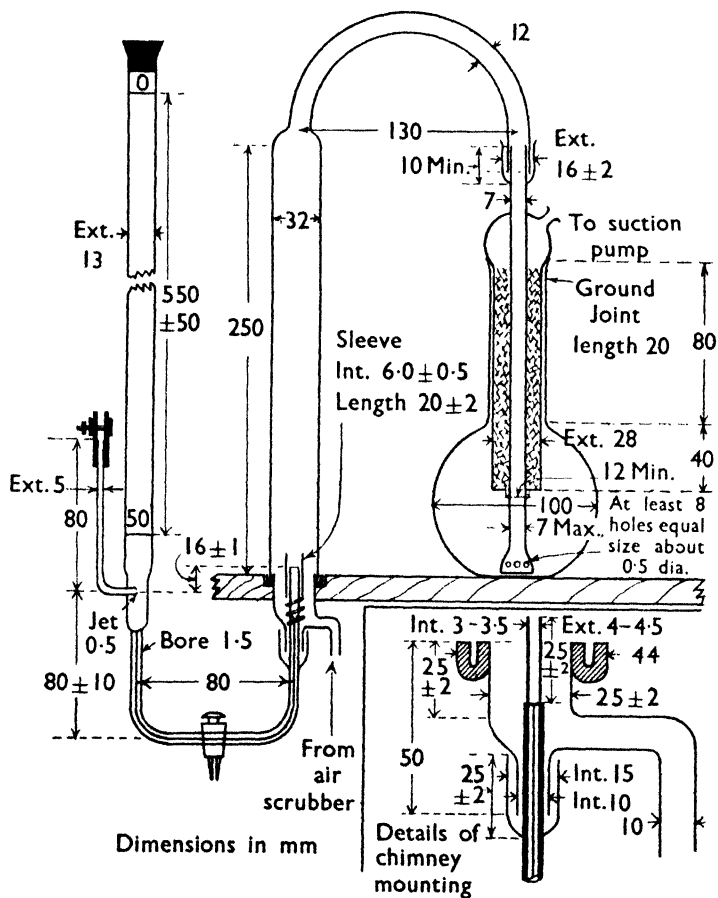
FIG. 44.—Total Sulphur in Refined Lower Boiling Products—Assembled Apparatus.

is placed in position, the burette reading being noted immediately. Smokeless combustion must be ensured by drawing sufficient air through the apparatus.

10 ml. at least of the stock solution is burnt and the chimney is removed at the same time as the burette reading is noted. The scrubber, the inlet tube and narrow portion of the chimney are rinsed into the flask and the hydrogen peroxide solution in the lute is also transferred thereto. The contents of the flask are titrated against

0·1 *N*. sodium carbonate solution, using bromophenol blue as indicator, with the intermediate grey shade as the end-point.

A blank test is carried out. The percentage by weight of sulphur is 0·802 $(V-v)/\rho M$, where V and v are the volumes of 0·1 *N*. sodium carbonate solution used in the test and required (on the basis of the blank test) if 4M/5 ml. of alcohol had been burnt, respectively ; ρ is the density of the sample and M is the number of millilitres of stock solution of sample burnt.

The test is said to be accurate within 0·01 in the percentage result. *Standard Methods* describes methods for testing the burette part of the apparatus ; and for using the method in the different circumstances which obtain in its adoption to the wide range of products for which it is applicable.

6. *Naphthalene*. *Standard Methods* (1929) describes a test for the determination of naphthalene, based on the formation of naphthalene picrate as described below ; experience has shown that in practice the method is of extremely limited applicability. It is probable that the test is very useful in the hands of one operator carrying out tests on successive samples in a closely delimited series, but gives unreliable results when the nature of the material under test is not well known. In these circumstances the test has not been retained in the 1938 edition of *Standard Methods*. The Standardization of Tar Products Tests Committee was unable to provide an alternative test which could be recommended for the 1938 edition, since whatever might be prescribed as to applicability, a standard test may be applied without entire regard to its limitations on its capabilities. The picrate method, submitted to the Committee in 1929 by L. J. White, is as follows :—

A delivery tube of 50 ml. is required, provided with a stop-cock and a nozzle reduced to a fine bore at the tip ; a 50-ml. burette with a nozzle so reduced can be conveniently used. Exactly 2 ml. of the sample is pipetted into the delivery tube and a freshly prepared solution of bromine in light petroleum (40°/60° fraction), containing 20 per cent. by volume of bromine, added drop by drop with gentle shaking until the spirit retains the bromine colour. The bromine colour must be permanent after allowing the delivery tube and contents to stand in the dark for ten minutes ; otherwise more bromine must be added until permanency of colour obtains after a further five minutes standing in the dark. A large excess of bromine must be avoided as it may interfere seriously with the subsequent proper precipitation of the naphthalene picrate. 10 ml. of acetone is then added and the liquid thoroughly mixed, any free bromine thus being removed. The contents of the delivery tube are now allowed to drop *very slowly* on to the surface of 250 ml. of a nearly saturated solution of picric acid in water, contained in a beaker, the upper portion of the liquid being stirred gently with a glass rod every few minutes.

The picric acid solution is prepared by diluting a saturated aqueous solution with one-twentieth of its volume of water. The time taken for the complete discharge of the liquid from the delivery tube should be about one hour. The delivery tube, including the exterior of the tip, is washed with a little acetone, the washings being run into the beaker, and the beaker and contents allowed to stand for two hours. Thereafter the liquid is filtered, under a gentle vacuum, through a 40 mm. filter paper placed on a 25 mm. perforated plate or through a Gooch crucible fitted with a disc of filter paper instead of the usual asbestos. The precipitated picrate is thoroughly washed with picric acid solution, the picrate being well pressed against the paper with a flat-ended glass rod, and finally sucked out for ten minutes with a good vacuum. The filter paper and precipitate are now transferred to a flask, heated to boiling point with distilled water, and the hot solution titrated with $N/50$ aqueous sodium hydroxide solution. 0·5 per cent. alcoholic solution of lacmoid, or a 0·04 per cent. aqueous solution of bromocresol purple is used as indicator. The colour change of the lacmoid solution is from reddish-brown in acid solution, to green in alkaline solution ; bromocresol purple solution changes in colour from yellow to violet. Each ml. of alkali is equivalent to 0·00256 g. naphthalene.

$$\frac{\text{The percentage by weight}}{\text{of naphthalene}} = \frac{100 \times 0{\cdot}00256 \times \text{ml. of alkali required}}{2 \times \text{specific gravity of sample}}$$

When the naphthalene content of the sample is below 1 per cent., the proper precipitation of the picrate is sometimes more difficult. If so, a weighed amount of pure dry naphthalene picrate (*e.g.* 0·1 g.) is dusted on to the surface of the picric acid solution in the beaker before making additions from the delivery tube. The volume of alkali corresponding to the weight of added naphthalene picrate (14·0 ml. for each 0·1 g.) is deducted from the volume used in the subsequent titration.

(i) *Rectification Test*

Tests to determine the quantity of unsaturated compounds are described under crude benzole (p. 181).

The rectification test purports to be a measure of the washing with sulphuric acid which the product has received during manufacture and determines the colour of the acid layer when the product is treated with 95 or 96 per cent. sulphuric acid. With the benzoles, toluoles and xyloles the hydrocarbon layer should remain practically colourless ; with the heavier solvents this test is generally not considered important or an acid of lower strength may be used. Varying results may be obtained if different volumes of acid are used in proportion to the volume of material treated ; moreover, a product stored for a period may give a less satisfactory result than the freshly prepared product. The colour of the acid layer is matched against a set of colour standards

made up, according to British practice, of varying amounts of standard potassium dichromate and cobalt sulphate solutions; alternatively, standard tintometer glasses equivalent to such standard colour solutions may be used. In America aqueous solutions of cobalt chloride and ferric chloride in a fixed ratio are used for the lighter colours and aqueous solutions of pure potassium dichromate for the higher standards. According to the Standard Method, a standard Lovibond tintometer may alternatively be used.

The sample is filtered and the first 10 ml. of filtrate is rejected; 5 ml. of a further portion of the filtrate is put in a stoppered cylinder of prescribed dimensions and 5 ml. of 95 per cent. sulphuric acid is added. The cylinder is shaken for *exactly* two minutes and allowed to stand for *exactly* ten minutes. Comparison is then made with the specified standard solution contained in a cylinder identical in all respects with that containing the sample and acid. The standard solutions may, as previously indicated, be replaced by the slides in the disc of a special comparator which The Tintometer Limited has designed for use in this particular test.

The Barrett Company (U.S.A.) adopts a somewhat comparable procedure, but a set of different colour standards. The following basic solutions are used :—

A. 59·50 g. $CoCl_2 6H_2O$ (nickel free) made up to 1 litre with a mixture of 25 ml. of 31 per cent. HCl and 975 ml. of water.

B. 45·054 g. $FeCl_3 6H_2O$ made up to 1 litre with a mixture of 25 ml. of 31 per cent. HCl and 975 ml. of water.

C. 3·5 volumes of solution A + 36·5 volumes of solution B + 90 volumes of water.

D. 3·5 volumes of solution A + 36·5 volumes of solution B (no water is added).

E. A solution of K_2CrO_4 saturated at 21°.

F. One volume of a solution of $K_2Cr_2O_7$ saturated at 21° + one volume of water.

The standard colour solutions are then made up according to the following table :—

Standard number.	Composition of solution.
0	Pure water.
1	1 volume solution C + 1 volume pure water.
2	5½ volumes solution C + 2 volumes pure water.
3	Solution C as such.
4	1 volume solution D + 1 volume pure water.
5	5½ volumes solution D + 2 volumes pure water.
6	Solution D as such.
7	5 volumes solution E + 2 volumes pure water.
8	Solution E as such.
9	7 volumes solution E + ½ volume solution F.
10	6½ volumes solution E + 1 volume solution F.
11	5½ volumes solution E + 2 volumes solution F.
12	1 volume solution E + 1 volume solution F.
13	2 volumes solution E + 5 volumes solution F.
14	Solution F as such.

The standard colour solutions are placed in a set of 15 one oz. capacity standard French square flint glass bottles, glass-stoppered, and sealed with a permanent seal to prevent evaporation. 7 ml. of 96 per cent. ±0·5 per cent. sulphuric acid is placed in a test bottle and 21 ml. of the material to be tested is added. The stopper is replaced and the bottle thoroughly and vigorously shaken for fifteen to twenty seconds, and then allowed to stand undisturbed for fifteen minutes, except with solvent naphtha, when a period of rest of five minutes only is allowed. If a hi-flash naphtha is being tested, 60 per cent. acid is used in place of the 96 per cent. acid, and again five minutes only allowed to elapse before the colour comparison is made. The resulting colour of the acid layer is compared with the set of standards in strong transmitted diffused daylight against a ground-glass background, and the number of the standard corresponding to the test-bottle is noted. When the colour of the test is between two standards, the sample is reported according to the darker one. Uniformity of colour of the acid layer is essential and may be obtained by slowly inverting the test bottle once or twice to mix carefully the acid layer. Great care must be taken that all the apparatus is perfectly clean.

(j) *Gum-forming Properties*

The acid-wash or rectification test is often referred to as a gumming test as far as motor benzole or petrol is concerned, but resinification of such a product bears no direct relation to the amount of unsaturateds, being influenced by traces of certain substances which do not cause an alteration in the colour of the sulphuric acid used in washing. Gum formation is hastened by exposure to ultra-violet light, but since this action is specific and varies with different qualities of benzole, the quantity of gum so formed is not an accurate criterion of the gumming tendencies of a benzole on storage.[1]

In addition to the gum formed on storage, there is of course that which may be present at the beginning of the storage period, in other words the "existent gum." There are consequently two Standard Methods, one for total potential and existent gum and one for existent gum alone. The former, developed as the result of international co-operation, was described at the time by Hoffert and Claxton [2] and with further particularization appears as the standard procedure in the 1938 edition of *Standard Methods*. It is applicable to benzoles distilling not more than 5 per cent. at 75° C., not less than 50 per cent. at 100° C. and not less than 95 per cent. at 145° C. In outline, the method consists in bubbling oxygen through the sample under controlled conditions, distilling off three-quarters of the sample and

[1] Hoffert and Claxton, *Motor Benzole, Its Production and Use*, London, 1st edn., 1931, p. 578; for survey of nature of resinification see *ibid.*, 2nd edn., 1938, p. 441.

[2] *Gas. J.*, 1932, **200**, 494.

evaporating the remainder to substantially constant weight, the weight of residue being the measure of the total quantity of gum formed by oxidation (potential gum) and present at the beginning of the test (existent gum).

The apparatus is shown in Fig. 45; those parts with which the sample in liquid or vapour form comes into contact must be made in one or other of an approved series of resistance glasses. The capillary tube flow-meter is calibrated by a prescribed method and the calibration is periodically checked.

As the previous history of the sample will have a bearing on the results, tests must not be carried out, or at least must not be regarded as satisfactory, unless the samples have been kept in amber-coloured glass bottles fitted with ground glass stoppers and cleaned before filling, in accordance with the method prescribed for cleaning the apparatus in connection with the test itself; furthermore, all samples intended for test must be kept in the dark until examined.

The oxidation process is extremely sensitive to traces of impurities; the whole of the apparatus is therefore rigorously cleansed before use, by filling the flask and condenser with strong acid-dichromate mixture, emptying after one or two hours, and washing first with water, then with caustic soda solution and finally with distilled water until the washings are no longer alkaline to litmus paper. The apparatus is then dried by warm air filtered through soda lime and cotton wool. The oxygen delivery tube and distillation head (shown in Fig. 45 and used at a later stage) are cleansed in exactly the same way.

100 ml. of the filtered sample is measured into the flask and the apparatus assembled. The water in the bath is raised to boiling-point within ten minutes. As soon as the water is boiling the oxygen is turned on and the rate adjusted to 37 ml. $\pm$ 2 ml. per minute by means of the tap on the flow-meter. The oxygen stream is maintained for three hours, while the water in the bath is kept vigorously boiling; the temperature of the water passing from the condenser is maintained at or below 25° C. by adjusting the rate of flow of the water.

The oxygen tube is withdrawn, the flask disconnected from the condenser, removed from the water-bath and connected to the distillation head. This is attached to an efficient condenser and the sample distilled into a 100 ml. graduated receiver fitted with a cork carrying a lead-off tube to convey gases evolved during the distillation away from any source of ignition. 75 ml. of distillate is collected, the flask disconnected and its contents poured into a dish made in one of the approved resistance glasses. Appropriate dimensions for this dish are given in the *Standard Methods*, as also are instructions for its preparation prior to the addition of the residue from the foregoing distillation. The dish is placed in a vigorously boiling water bath

where it remains for one and a half hours, protected from dust. It is then transferred to an oven and maintained at 98° to 105° C. for an hour, after which it is cooled in a dust-free atmosphere and weighed to an accuracy of ± 0·2 mg. The gum content is expressed in mg. per 100 ml. of sample. The test is said to be accurate within 1 mg., but the text of the Standard Method must be consulted, as various precautions must be taken to eliminate the effect of what might seem to be comparatively insignificant factors. The original text also emphasizes the extremely dangerous and explosive conditions under which the test must necessarily be performed and the precautions which must be taken throughout the test in order to minimize the risk of accident or the effects of an accident.

The determination of the existent gum or, as formerly termed, the residue on evaporation, is really the latter part of the foregoing method, carried out on 100 ml. of the sample as received instead of after prior refluxing in the presence of oxygen. In other words, 75 ml. of distillate is collected from 100 ml. of sample, the residue in the flask is evaporated in one of the weighed dishes and the gum dried under the same prescribed conditions.

The content of existent gum may however be required on samples which are not tested for total gum in ordinary practice, viz. on samples distilling less than 50 per cent. at 100° C. and/or less than 95 per cent. at 145° C. In such cases evaporation on the water-bath is continued for a longer period than the one and a half hours prescribed earlier, and actually goes on until evaporation is complete.

7. *Phenols.* Refined lower boiling products frequently contain tar phenols, but only in limited amount. The usual principles of *Standard Methods* are employed, viz. extraction with caustic soda, boiling of the alkali extract to remove neutral oils and bases, liberation of the phenols by acidification and measurement of the volume of the phenols.

250 ml. of the sample is taken in a stoppered separating funnel and shaken therein with 25 ml. of 10 per cent. caustic soda solution. After five minutes of vigorous shaking and subsequent settlement, the alkaline layer is run off into a beaker; if the pyridine bases are to be determined (see p. 282) the upper layer is reserved for the purpose.

The contents of the beaker are boiled vigorously for two minutes and transferred, after cooling to laboratory temperature, to a standard phenols flask; this flask has an approximate capacity of 150 ml. and a neck graduated from 0 to 10 ml. in tenths of a ml. Methyl orange is added and then concentrated hydrochloric acid until distinct acidity is just indicated after vigorous shaking together of the two layers. The contents of the flask are kept cool during acidification.

Just sufficient powdered sodium chloride is added to saturate the

aqueous layer and leave a few particles undissolved; the phenols are brought into the graduated portion of the flask by adding saturated salt solution. After settlement (preferably overnight) the volume of phenols is noted.

The method as described is applicable to samples containing 1 per cent. or less of phenols. Extensions to the Standard Method are available for use when the phenols content is between 1 and 3 per cent.

8. *Pyridine Bases.* The Standard Method is carried out on the phenols-free sample, the pyridine bases being extracted with dilute acid, the extract neutralized and steam distilled and the bases in the distillate titrated with acid.

The 250 ml. of sample separated from the alkali wash, according to (7) above, is shaken for two minutes with 20 ml. of 25 per cent. sulphuric acid. After standing until separation is complete, the lower layer is run into a round-bottomed flask; 100 ml. of water and 50 ml. of 20 per cent. caustic soda solution are added, the mixture being kept cool throughout.

The mixture is distilled in the apparatus shown in Fig. 34, except that the receiver is a 250 ml. flask; 100 ml. of distillate is collected and three drops of 0·1 per cent. phenolphthalein solution (made with 50/50 alcohol/water mixture as solvent) are added. If a purple colour develops, the mixture is titrated with 0·1 *N.* hydrochloric acid until colourless; this liquid (or if no purple colour develops on the addition of the phenolphthalein, the liquid after that addition) is titrated with *N.* hydrochloric acid after adding 0·3 ml. of a 0·04 per cent. solution of bromophenol blue.

If only one drop of acid is required pyridine bases are reported absent; otherwise the percentage *w/v* expressed as pyridine is $0{\cdot}4 \times 0{\cdot}079 \times V$ where V is the *N.* hydrochloric acid titre.

(k) *Volatility*

According to Hoffert and Claxton[1] the "average volatility" of a motor fuel such as motor benzole is a very ill-defined term, and no method of measuring this property has yet met with universal approval. The temperatures at which various percentages distil over in standard distillation tests are frequently taken as a criterion, although the inaccuracies, due both to the loss of volatile constituents and thermometric lag, render the results of doubtful value. For the determinations of starting volatility and average or equilibrium volatility the work of Brown[2] and of Bridgeman[3] should

[1] *Motor Benzole, Its Production and Use*, London, 1931, p. 485.

[2] Brown, *et al.*, *Ind. Eng. Chem.*, 1930, **22**, 278, 649, 653, 662, 672.

[3] Bridgeman, Aldrich and White, *J. Soc. Automotive Eng.*, 1929, **24**, 488; Bridgeman, *ibid.*, 1929, **25**, 44; cf. *Amer. Petroleum Inst. Bull.*, 1929, **10**, No. 2, Sect. 2, p. 124.

be consulted. To obtain a general indication of the uniformity of evaporation and of the nature and amount of the residual oil after evaporation, 10 ml. of the motor benzole to be tested may be placed in a clean dry watch-glass which is then allowed to stand in an open situation in the laboratory at a room temperature of 15° to 20°; a piece of black paper should be placed under the watch-glass during the test.[1]

(1) *Flash-point.*

The flash-points of lower-boiling fractions of coal tar are determined in the Abel apparatus for oils flashing between 66° F. and 90° F., and in the same apparatus employing a modified procedure for oils flashing between 90° F. and 120° F. For the accurate determination of the flash-points of the more volatile products, such as benzole, special apparatus such as that described by Ormandy and Craven[2] is required. In deciding what method shall be used it must be remembered that in certain circumstances it is obligatory to use the Abel apparatus in the manner prescribed by petroleum legislation. *Standard Methods*, in consequence, reproduces verbatim the test as described in the schedules to the Petroleum (Consolidation) Act, 1928, for use in connection with oils flashing between 66° F. and 90° F. The Act is not concerned with oils flashing below 66° F. as in a category different from those flashing between 66° F. and 90° F., but there has grown up a regular demand for determinations of flash-points below 66° F. and a modification of the statutory technique is therefore provided in *Standard Methods* to cover oils flashing between 35° F. and 66° F.

The modification consists first in preparing the flash-point apparatus in the usual manner but filling it with water at 90° F. instead of 130° F. Secondly, the sample must have been cooled to 32° F. or lower for at least two hours and with occasional shaking. The sample so cooled is well shaken and poured into the cup to the prescribed level, the cup then being placed in position in the flash-point apparatus without delay. The subsequent procedure is normal except that the test flame is applied first when the temperature reaches 35° F. and thereafter once for each rise of one degree.

The flash-point is affected by the presence of water; when the test is required on the sample freed from water, drying is effected by means of finely powdered plaster of Paris, about 100 g. of which is placed in a dry wide-mouthed stoppered bottle having a capacity of about 450 ml. and containing about 250 ml. of the sample. The bottle is stoppered and shaken thoroughly for ten minutes. Sufficient of the dried and settled sample is decanted for the test.

[1] Dieterich, *loc. cit.*

[2] *J. Inst. Petroleum Tech.*, 1922, **8**, 145; 1923, **9**, 33.

The 1928 Act makes no mention of corrections for barometric pressure, though in view of the influence of this factor and the importance of the issues which can be at stake, a definite pronouncement would have been beneficial. Presumably it is assumed that the test is carried out when the atmospheric pressure is normal. In practice, the observed flash-point may be corrected by adding or subtracting 0·63° F. for each 10 mm. by which the prevailing barometric pressure is below or above 760 mm. as the case may be.

(m) *Distinction and Estimation of Coal Tar Benzene in Admixture with Petroleum Benzine and Similar Products*

It is frequently necessary to distinguish between the light hydrocarbons of coal tar and those from petroleum, lignite and shales. This can usually be done by determining the sp. gr., which is never below 0·870 for coal tar benzoles and seldom exceeds 0·750 for the other products in question. Their different behaviour in the presence of nitro-sulphuric and fuming sulphuric acid is also characteristic, and can be employed for the detection and quantitative determination of any admixture of coal tar benzole with petroleum benzine and similar substances; a comparative table has been given by Allen.[1] Gawalowski [2] has pointed out that picric acid is almost insoluble in petroleum benzine, but dissolves readily in benzene, forming a dark yellow solution. Concentrated solutions of picric acid in benzene are precipitated when added to petroleum benzine. Holde [3] utilizes the behaviour of the two classes of hydrocarbons in the presence of coal tar pitch as a test for the adulteration of one with the other. He extracts powdered pitch completely with high-boiling petroleum and, after drying, preserves it as a reagent. Enough of this to cover the point of a knife is placed on a small filter and 5 ml. of the liquid to be tested is poured over it. As little as 5 to 10 per cent. of benzene in petroleum benzine of sp. gr. 0·64 to 0·70 can be detected by the yellow coloration of the filtrate. By making comparative tests the approximate quantity of added benzene can be estimated from the intensity of the coloration.

Inversely, the quantity of petroleum benzine in benzole can be determined by observing the coloration with pitch and comparison with that given by standard mixtures. Weiss [4] prepares a residue from pitch which would also appear to be suitable for this purpose. The pitch is dissolved in benzole, the free-carbon filtered off, the benzole removed by distillation, and the residue completely extracted

[1] *Chem. News*, 1879, 40, 101.
[2] *Chem. Centr.*, 1897, 1, 1038.
[3] *Fischer's Jahresber.*, 1895, 554.
[4] U.S. Pat. 1355099, 1920.

with petroleum naphtha. The final residue is insoluble in petroleum products, but readily soluble in benzole or coal tar naphtha. Schwarz [1] tests petroleum spirit by adding to 5 ml. of the sample, 2 ml. of a mixture of equal volumes of aniline and 95 per cent. alcohol; if the spirit is free from benzene the aniline separates out as a layer, but as little as 5 per cent. of benzene keeps the aniline in solution and the mixture remains clear. The test may be particularly applied to the 80° to 110° fraction. Formánek, Knop and Korber [2] describe a method based on the solubility of certain indanthrene dyestuffs in aromatic hydrocarbons, these dyestuffs being insoluble in non-aromatic hydrocarbons; saturated solutions of these dyestuffs in hydrocarbon mixtures are compared with solutions of known aromatic content. Thole [3] considers that the method is not sufficiently sensitive for the accurate determination of aromatic hydrocarbons in petroleum spirit. For the detection and estimation of benzene, Stock,[4] in common with Pritzker and Jungkunz,[5] employs the nickel cyanide method. According to the latter the reagent is made up as follows:—

20 ml. of concentrated ammonia solution is added to a mixture of 5 g. of recrystallized nickel sulphate in 20 ml. and 2·5 g. of potassium cyanide in 10 ml. of water. After standing for thirty minutes at 0° the solution is filtered through glass wool, and 80 ml. of the filtered solution is acidified with 50 per cent. acetic acid until a permanent cloudiness is just produced.

To this mixture is added 1 to 1·2 g. of benzene, or up to 10 g. of a benzene mixture. The mixture is well shaken for five minutes and the precipitate separated quantitatively by filtration. The precipitate is finally washed once or twice with cold water, followed by washing with alcohol and ether, dried for two to four hours over sulphuric acid and weighed. The percentage of benzene is calculated from the formula $Ni(CN)_2NH_3C_6H_6$, with which the analysis of the precipitate gives good agreement.

Cook [6] describes a somewhat elaborate method for the determination of small quantities of benzene according to which a brown coloration or black precipitate is produced by the reaction of a 0·5 per cent. ferrous sulphate solution and a one per cent. solution of hydrogen peroxide with benzene; the precipitate is dissolved in nitric acid and compared colorimetrically with standard solutions. The so-called Drakorubin test [7] depends upon the solubility of Drakorubin resin,

[1] *Chem.-Ztg.*, 1922, **46**, 401.
[2] *Chem.-Ztg.*, 1917, **41**, 713, 730.
[3] *J. Soc. Chem. Ind.*, 1919, **38**, 39 T.
[4] *Farben-Ztg.*, 1930, **35**, 897.
[5] *Chem.-Ztg.*, 1924, **48**, 455; *cf.* Hofmann and Höchtlen, *Ber.*, 1903, **36**, 1149.
[6] *Ind. Eng. Chem.*, 1932, **4** (*Anal.*), 406.
[7] Dieterich, "Die Analyse und Wertbestimmung der Motorbenzine und -benzole und des Motorspiritus des Handels," *Z. des Mitteleuropäischen Motorwagen-Vereins*, Parts 9 and 10, 1915.

either in liquid form or prepared as test-papers,[1] in benzene, but not in petroleum benzine. According to Formánek [2] this test must be applied with discrimination, since Drakorubin is also soluble in methyl, ethyl and amyl alcohols, carbon disulphide, ether and acetone. According to Wegner,[3] Kattwinkels' test,[4] in which is employed a solution of sulpho-acetic acid in acetic anhydride, is not reliable.

II. CARBON DISULPHIDE

For tests for carbon disulphide, as for example as an impurity in benzole, see p. 258.

The requirements for British Standard carbon disulphide are as follows [5]: The carbon disulphide must be clear, colourless and free from suspended matter and visible water and consist essentially of carbon disulphide (CS_2). The sp. gr. at 15·5°/15·5° must not be lower than 1·270 nor higher than 1·274, and at 20°/20° must not be lower than 1·265 nor higher than 1·269. On distillation in standard apparatus, employing a standard procedure, at least 95 per cent. must distil below 46·4° at 760 mm. pressure. Evaporation of 100 ml. of the carbon disulphide to dryness in a weighed platinum or silica basin on a water-bath and further heating of the residue for one hour in an oven at 98° to 100° must not leave more than 0·01 per cent. by weight. Shaking 10 ml. of the carbon disulphide with 10 ml. of freshly boiled and cooled distilled water must give an aqueous extract which is not acid to methyl red. 100 ml. of the carbon disulphide should not decolorise 1·0 ml. of *N*/100 iodine solution when shaken vigorously with it in a stoppered glass cylinder, this test being a limiting test for hydrogen sulphide.

III. COUMARONE RESINS

(a) Preparation

Coumarone resins are a by-product of the sulphuric acid washing of commercial benzole and solvent naphtha, and consist of the polymerized products of coumarone, indene, styrol, and its homologues and cyclopentadiene. A well-annotated account of the preparation, properties and application of coumarone resins is given in the publication of Scheiber and Sändig.[6] The work of Kraemer and

[1] Berger, *Zentr. Gewerbehyg.*, 1928, **15**, 227; *Chem. Zentr.*, 1928, **99**, ii. 1594.
[2] *Z. angew. Chem.*, 1918, **31**, Ref. 62. [3] *Chem.-Ztg.*, 1925, **49**, 348.
[4] *Chem.-Ztg.*, 1925, **49**, 57. [5] *British Standards Institution, B.S.* 662, 1936.
[6] *Artificial Resins*, Scheiber and Sändig, trans. by Fyleman, London, 1931.

Spilker,[1] Marcusson,[2] and Wolff,[3] should also be consulted. The polymerizable constituents of the light coal-tar fractions occur as follows :—

Fraction under 160° .	. Styrols and cyclopentadiene (b.p. 42·5°).
,, 168° to 175° .	. Coumarone (b.p. 170° to 171°).
,, 176° ,, 182° .	. Indene (b.p. 182·4°).
,, 182° ,, 200° .	. Methylcoumarones.
,, 200° ,, 210° .	. Methylindenes.
,, 215° ,, 225° .	. Dimethylcoumarones.

On treatment with sulphuric acid, cyclopentadiene forms insoluble black resins ; styrol produces viscous oils of high boiling point and the homologues of coumarone and indene, when polymerized with these two substances, give soft products. The highest quality products are obtained from coal-tar fractions rich in coumarone and indene, and particularly from the fraction boiling between 160° and 185°. The properties of the coumarone resin depend upon the nature of the raw material, the strength and amount of sulphuric acid employed, the temperature at which polymerization is allowed to proceed and the time of contact of naphtha and acid. The progress of the polymerization process can be followed by determinations of the sp. gr. of the oil, which rises as polymerization proceeds. After polymerization is complete, a mixture of acid resin (insoluble in solvent naphtha) and acid separates on standing and later is carefully removed. The solvent naphtha containing the coumarone resin is now washed, neutralized with alkali, and then thoroughly washed with water to remove any remaining acids and salts which would otherwise cause discoloration and deterioration of the resin during the subsequent distillation. The washed oil is directly distilled with steam under reduced pressure, the solvent naphtha distilling over first, followed by some naphthalene and finally by a heavy oil which boils between 320° and 330° at ordinary pressure. Distillation is continued until a sample of the residual resin is of a sufficiently high melting point. The product is eventually purified and its hardness and other properties adjusted by a variety of methods to suit requirements.

(*b*) Properties

Commercially, coumarone resins vary from viscous liquids to solids of a hard brittle character, and in colour from very pale yellow, through yellow, brown, and dark brown to black. They have been classified

[1] *Ber.*, 1890, **23**, 78, 84, 3169, 3269; 1896, **29**, 552; 1900, **33**, 2257; 1901, **34**, 1887; 1903, **36**, 645.

[2] *Chem.-Ztg.*, 1919, **43**, 93, 109, 122; *Mitt. Materialprüf.*, 1920, **38**, 69.

[3] *Farben-Ztg.*, 1917, **22**, 917, 945; 1918, **23**, 12, 307.

	Pale. 10 per cent. solution not darker than 15 g. of $K_2Cr_2O_7$ per litre of 50 per cent. H_2SO_4.	*Pale Brown.* 3½ per cent. solution not darker than 15 g. of $K_2Cr_2O_7$ per litre of 50 per cent. H_2SO_4.	*Brown.* Artificial light penetrates 10 per cent. solution.	*Dark.* Artificial light penetrates 5 per cent. solution.	*Black.* Artificial light fails to penetrate 5 per cent. solution.
Very hard. Softening point over 50°	1	2	3	4	5
Hard. Softening point between 40° and 50°	6	7	8	9	10
Medium hard. Softening point between 30° and 40°	11	12	13	14	15
Soft. Softening point below 30°. Immersion period in nail test more than 500 seconds	16	17	18	19	20
Viscous. Immersion period between 100 and 500 seconds	21	22	23	24	25
Liquid. Immersion period less than 100 seconds	26	27	28	29	30
Residues containing coumarone resins	31	32	33	34[1] (29 and 30)	
	27 to 35 per cent. resin content.	20 to 27 per cent. resin content.	Below 20 per cent. resin content.	20 to 40 per cent. resin contents. Technically free (not over 1 per cent.) from sodium phenolate. Maximum water content, 2 per cent.	

[1] For Class 34 there are special specifications which refer to the raw material (in the washing of benzole, toluole, or mixtures of these). There are also stipulations with regard to water content (maximum, 2 per cent.); boiling point (a maximum of 10 per cent. may distil below 200°); naphthalene content (free from naphthalene as far as possible, maximum 8 per cent.); resin content (up to 40 per cent.), and sodium phenolate (not over 1 per cent.).

into thirty-four different classes [1] according to hardness and colour as indicated by numbers in the previous table.

Additional classes have been elaborated to distinguish further the very hard resins, these being characterized with the suffix /50 to their class number if with a softening point between 50° and 55°, with the suffix /55 if softening between 55° and 60°, by the suffix /60 if softening between 60° and 65°, and so on. The pale classes (1 and 6) have also been more closely defined by comparison with weaker solutions of potassium dichromate in 50 per cent. sulphuric acid than that shown in the above table. The prefixed 01, 001, 0001, and 00001 before the appropriate softening point (*e.g.* 01/50, 001/60, 0001/65), denotes the range of decreasing colour of these products according to defined potassium dichromate—50 per cent. sulphuric acid solutions. Five classes are distinguished in America,[2] namely :—

Rubber grade S	m.p.,	50° to 65°
Medium soft	,,	65° ,, 85°
Rubber grade H	,,	85° ,, 100°
Medium hard	,,	100° ,, 135°
Varnish grade	,,	135° ,, 150°

Colour definitions in this case are referred to the colour ranges of colophony (rosins).

Solid coumarone resins have a sp. gr. of about 1·2 to 1·3; an odour resembling gum benzoin; acid ratios of between 1 and 20; saponification values of from 1 to 25; and iodine values of from 23 to 29.

Coumarone resins are readily soluble in benzene and its homologues, and in solvent naphtha; and soluble in turpentine, acetone, ether, ethyl acetate, amyl acetate, carbon tetrachloride, chloroform, trichlorethylene and carbon disulphide. They are not completely soluble in light petroleum spirits, but become so on addition of benzene; they are only slightly soluble in alcohol.

According to Marcusson [3] their colour depends on the proportion of constituents insoluble in acetone (acid resin). The melting-point rises with an increasing proportion of constituents insoluble in alcohol-ether. The table on p. 290 shows the behaviour of the various classes of coumarone resins to alcohol-ether and acetone.

Coumarone resins can be melted together with pitch, asphalt and natural resins in all proportions; paraffin wax, ceresine and paraffin

[1] Report on the work of the Sub-Committee on the Classification of "Coumarone Resins," *Kunststoffe*, 1919, **9**, 190; *C*, 1920, **11**, 450.

[2] Cf. *Synthetic Resins and their Plastics*, Ellis, New York, 1923, p. 40.

[3] *Chem.-Ztg.*, 1919, **43**, 93, 109, 122; *C*, 1919, **IV**, 14; *Mitt. Materialprüf.*, **38**, 69; *C*, 1921, **IV**, 1230.

oil dissolve limited quantities only. Coumarone resins decompose on heating to 300° to 400°, yielding mainly coumarone or depolymerized paracoumarone together with indene, hydrindene and small amounts

Quality No.	External character.	Behaviour with alcohol-ether.		Insoluble in acetone.	
		Soluble.	Insoluble.	Organic.	Inorganic.
	Very hard—	Per cent.	Per cent.	Per cent.	Per cent.
1	Pale	47	53·0	nil	nil
2	Pale brown	48	52·0	,,	,,
5	Black	64	17·0	8·3	7
	Hard—				
6	Pale	56	44·0	nil	nil
7	Pale brown	58	42·0	,,	,,
	Medium Hard—				
11	Pale	67	32·0	,,	,,
15	Black	55	34·0	11·0	,,
	Soft—				
16	Pale	69	30·0	nil	,,
20	Black	69	15·5	12·5	,,
	Viscous—				
23	Brown	84	1·0	2·0	5
	Liquid—				
28	Brown	73	7·3	2·0	nil
30	Black	76	4·7	4·4	3

of phenol. As impurities the resins may contain acid resins, tar oils, adulterants of a pitchy or asphaltic character, mineral matter, and, due to the methods of manufacture, water, alkali and sulphuric acid.

(*c*) Detection of Coumarone Resins

Scheiber and Sändig [1] describe the following reactions for the detection of coumarone resins :—

1. To differentiate coumarone resins from coal-tar and wood-tar pitches and mineral oil asphalt, which are occasionally offered as dark coumarone resins, the solubility of the sample in acetone should be determined. All qualities of coumarone resins are either completely soluble or leave only a very small amount of residue; pitchy residues and mineral oil asphalts are only slightly soluble.

2. In contradistinction to aldehyde resins, coumarone resins are freely soluble in petroleum spirit.

3. Natural resins have usually higher melting-points than coumarone resins and give higher acid, saponification and iodine values; the former are also optically active, whereas coumarone resins are inactive.

4. Coumarone resins are insoluble in alkalis. Saponification will thus allow of the distinction between coumarone resins and fatty oils, and acid resins such as colophony, phenol-aldehyde resins and the like. A further distinguishing test from

[1] *Loc. cit.*, p. 250.

phenolic resins is by ignition with soda-lime. According to Marcusson the test may be carried out as follows :—

> 1 g. of the resin is heated with 3 to 5 g. of soda-lime for two hours at 260° in an oil bath and the mixture then extracted with warm water. If considerable quantities of phenols are liberated on acidification of the solution with mineral acid, a phenolic resin is present.
>
> On adding a few drops of freshly-prepared diazobenzene solution to the above alkaline solution an intense red coloration is produced, or a red precipitate of an azo-dyestuff. Coumarone resins yield only a slight precipitate of resin acids, and a weak red coloration with the diazobenzene solution.

5. Dry distillation of coumarone resin yields a distillate, of which the main fraction boils between 168° and 180°. Coumarone and indene in the latter can be identified as picrates or bromides : coumarone picrate, m.p. 102° to 103° ; monobromide, m.p. 39° ; dibromide, m.p. 86° ; indene picrate, m.p. 98°, b.p. 179·5° to 180·5° ; indene dibromide, m.p. 43° to 45°. The 170° to 180° fraction, on adding a few drops of concentrated sulphuric acid, gives a viscous polymerized product. Natural resins give only small quantities of the 168° to 180° fraction, which is free from coumarone and indene.

6. 1 ml. of a 10 per cent. chloroform solution of the resin is diluted with a further 6 ml. of chloroform and 1 ml. of glacial acetic acid added. To the resulting solution, 1 ml. of a 10 per cent. chloroform solution of bromine is added, the mixture well shaken and allowed to stand. Coumarone resin produces a permanent red coloration, but resinolic acids give a reddish-yellow colour, changing to pure yellow on standing for twenty-four hours.[1]

For the detection of coumarone resins in varnishes the work of Wolff should be consulted.[2]

(*d*) Testing of Coumarone Resins

The methods commonly used for the testing of coumarone resins are mainly those of the German War Committee for Fats and Oils, and applied by the Cumaronharz-Verband G.m.b.H. of Bochum.[3]

1. **Colour.**—The colour of coumarone resins is expressed by comparison with a standard solution of potassium dichromate in dilute sulphuric acid. 1 to 1·5 g. of the resin is weighed into a test-tube correct to 0·1 g. and 1 ml. of ordinary purified water-white benzole added for each 0·1 g. of resin. For this purpose a small measuring cylinder graduated in 0·2 ml. may be employed. In the examination of soft or viscous samples a small tared glass rod or wooden splint may be used and weighed with the test-tube. The resin is dissolved by shaking, with or without warming. With many resins this 10 per cent. solution is directly suitable for comparison ; with darker resins it must be diluted with benzole until a solution of a suitable depth of colour is obtained. For the comparator solution

[1] Cf. *Synthetic Resins and their Plastics*, Ellis, New York, 1923, p. 54.
[2] *Farbe und Lack*, 1928, 85. [3] Cf. *Kunststoffe*, 1919, 9, 190.

15 g. of pure potassium dichromate is dissolved in 1 litre of pure 50 per cent. sulphuric acid. Comparison of the freshly-prepared and shaken resin-benzole solution with the standard dichromate solution is made, using two thin-walled test-tubes of the same diameter, placed side by side in transmitted daylight with the sky as a background, attention being directed to depth of colour and not to the tint. Colour ranges are indicated in the classification table on p. 288.

For pale and clear resins the following additional colour gradations have been adopted :—

Types 01. 06. but not in classes 11, 16, 21 and 26	10 per cent. benzole solution of resin not darker than a comparator solution containing 3·0 g. of potassium dichromate per litre of 50 per cent. sulphuric acid.
Types 001. 006. but not in classes 11, 16, 21 and 26	10 per cent. benzole solution of resin not darker than a comparator solution containing 1 g. of potassium dichromate per litre of 50 per cent. sulphuric acid.
Type 0001. but not in classes 6, 11, 16, 21 and 26	25 per cent. benzole solution of resin not darker than a comparator solution containing 1 g. of potassium dichromate per litre of 50 per cent. sulphuric acid.
Type 00001. but not in classes 6, 11, 16, 21 and 26	50 per cent. benzole solution of resin not darker than a comparator solution containing 1 g. of potassium dichromate per litre of 50 per cent. sulphuric acid.

The colour groups " brown," " dark," and " black " are observed by the transmission of artificial light of about 50 c.p. from an incandescent electric lamp or benzole-heated mantle through the freshly-prepared benzole solution contained in a test-tube of 15 mm. internal diameter. The test-tube is placed about 50 cm. from the source of light, lateral illumination being cut off by holding the test-tube between two fingers or by placing it in a wooden block in which two small slots are cut opposite each other.

2. **Determination of Hardness and Consistency.**—The softening points of the hard resins up to type 15 are determined according to the Kraemer Sarnow Method (p. 417). For the soft, viscous or liquid types the so-called " nail test " is used, which defines the period of immersion of a 5-in. round wire nail (known commercially as 23/60 nails, 130 mm. in length, and 23 to 24 g. in weight) in the resin maintained at exactly 20°. The sample of resin is placed in a vessel of at least 8 to 10 cm. diameter to a height of at least 15 to 20 cm., and maintained at 20°, by immersion, if necessary, in water at that temperature, in which it must stand for a sufficient time (often for six to twelve hours).

The nail must also be at the same temperature and must not be

warmed by holding in the hand for any length of time. The nail is held by the head between the thumb and index finger of the left hand in a vertical position over the sample of resin, whilst with the right hand a simple wire loop of about 10 mm. diameter is slipped over the nail from below nearly up to the head to maintain it in a vertical position when liberated. The number of seconds is counted which elapse between the moment when the nail released by the left hand just disturbs the surface of the resin, and that at which the nail has sunk so far into the resin mass that the head just touches the surface. The viscosity of the dark, viscous and liquid varieties may be determined in the viscometer described by R. Fischer.[1]

3. **Steam Distillation.**—If the nail test gives a figure of less than five seconds the material is probably not a true coumarone resin, but a residue or oil containing coumarone or substances of a like character. Coumarone resin types 31 to 34 are arranged according to the resin content of the residue as determined by means of steam distillation. 100 g. of the sample is weighed into a glass distillation flask or retort of 350 to 500 ml. capacity, and the vessel heated in an oil bath up to a temperature of 200°. 50 ml. of benzene or xylene may be added to prevent frothing over of the resin. The thermometer bulb is placed just below the side tube of the flask and a 25 ml. measuring cylinder used as a receiver. At 200° the distillation is interrupted and the quantities of aqueous and oily distillates measured and recorded as percentages.

The thermometer is now lowered into the resin, the receiver replaced by a larger one, and dry steam passed through the flask and heating continued so that the temperature of the resin rises to between 190° and 200°. Distillation is continued until 125 ml. of water have been collected. During steam distillation naphthalene condenses in the condenser. The naphthalene is transferred to a porcelain dish by stopping the cooling water for a short time, and after solidifying again it is dried on a tile and weighed. The residue in the flask is weighed and gives directly the percentage of resin. If less than 35 per cent. of resin is obtained the sample consists of residues or oils containing coumarone resins. The softening point of the residual resins should be about 80°. Coumarone resins from benzole washing should contain less than 2 per cent. of moisture, on distillation up to 200° give not more than 10 per cent. of distillate, and the naphthalene content should be a minimum, but in any case should not exceed 6 per cent.

4. **Determination of Sodium Phenolate.**—Coumarone resin residues, type 34, should not contain over 1 per cent. of sodium phenolate. To determine the amount present in a sample, 50 g. of the resin is

[1] *Chem.-Ztg.*, 1920, 44, 622.

dissolved in 200 ml. of benzene in a separating funnel, 300 to 350 ml. of water added, and the whole well shaken. The phenolates dissolve in the water. After standing to allow separation, which requires some time but is quite sharp, the aqueous layer is withdrawn into a 1 litre flask, and the benzene solution shaken with a further 200 ml. of water, and this treatment repeated with a similar quantity of water, if necessary. Qualitative tests with bromine water or other phenol indicators will determine this procedure. The combined aqueous solutions are then made up to 1 litre, filtered, and the phenol in the filtrate determined by Koppeschaar's method, which is as follows :—

10 ml. of the phenol solution and 50 ml. of a potassium bromide-potassium bromate solution, containing 7 g. of potassium bromide and 1·6702 g. of potassium bromate per litre, are placed in a bottle or flask fitted with a well-ground glass stopper ; 15 ml. of 50 per cent. sulphuric acid is added, and the stoppered vessel shaken vigorously. Tribromophenol and tribromophenol bromide separate. After ten to fifteen minutes, 10 to 15 ml. of potassium iodide solution, containing 125 g. per litre, is added, the vessel again shaken and after a few minutes the liberated iodine is titrated with $N/10$ sodium thiosulphate solution using starch solution as indicator.

1 ml. of $N/10$ sodium thiosulphate solution is equivalent to 0·001934 g. of sodium phenolate or 0·001567 g. of phenol. Any cresol which may be present is calculated as phenol. The relation between the potassium bromide-potassium bromate solution and the $N/10$ sodium thiosulphate solution is determined by a blank test.

5. **Determination of Impurities.**—(a) *Water.* 100 g. of the sample of resin is dissolved in 200 ml. of xylene or purified commercial benzole and distilled in a flask until a clear distillate is condensed. The number of ml. of water separating in the collecting cylinder corresponds directly to the percentage of water in the sample. Coumarone resins should be substantially free from water.

(b) *Alkali.* Owing to the methods of manufacture, coumarone resins frequently show an alkaline reaction. The alkali content may be determined by boiling the sample with distilled water, and titrating the alkali in the aqueous extract with standard acid solution, using phenolphthalein as indicator.

(c) *Free and Fixed Sulphuric Acid.* According to Wolff[1] many types of coumarone resins contain considerable quantities of acid constituents, 30 resin samples giving acid ratios of about 1 to 20, and saponification values of about 1 to 25. Apart from free sulphuric acid, water-soluble sulphonic acids and other sulphuric acid-containing components which are dissociated by, but insoluble in water[2] may be

[1] *Farben-Ztg.*, 1917, **22**, 917.

[2] Marcusson, *Chem.-Ztg.*, 1919, **43**, 110.

present. To determine the free sulphuric acid, Wolff states that 10 to 20 g. of the resin is dissolved in 50 ml. of neutral benzene or xylene and shaken repeatedly with warm water; three extractions each with 20 ml. of water generally suffice. The aqueous extracts are bulked, filtered, acidified with a few drops of hydrochloric acid and the sulphuric acid precipitated with barium chloride at 80°. The solution should not be boiled, since decomposition of the sulphonated substances may result and liberate more sulphuric acid. The water-soluble fixed sulphuric acid is determined in the filtrate from the above determination. The solution is made alkaline with a few millilitres of concentrated sodium hydroxide solution, evaporated to dryness, a small amount of potassium nitrate added and the dry mass fused. It is then redissolved in water and hydrochloric acid and the sulphuric acid precipitated as barium sulphate. A check on the nature of the water-soluble acidity may be obtained by titration of the aqueous extract with $N/10$ sodium hydroxide solution. The total sulphuric acid (the sum of the free sulphuric acid and the soluble and insoluble fixed sulphuric acid) is determined by saponification of 15 g. of the sample with $2N$ alcoholic potash, evaporating the solution and melting the residue, for which purpose Marcusson adds a small amount of potassium nitrate. The melt is dissolved in water, acidified with hydrochloric acid, and the solution, filtered from insoluble resin, precipitated with barium chloride. Wolff found 0·35 and 1·17 per cent. of sulphuric acid (expressed as SO_3) in two resins; the water-soluble sulphonic acids in six samples varied from 0·18 to 1·4 per cent., and the sulphonic acids insoluble in water in ten samples from 0·09 to 2·1 per cent. Marcusson considers that not only the water-soluble free and combined sulphuric acid is injurious in the resins, but also the water-insoluble sulphonic acids and other sulphuric acid-containing components which may liberate acid on ageing or coagulation of the resin, for example on treatment with salt solutions. Coumarone resins containing such acid constituents act as rust promoters rather than rust preventatives, and the occasional thickening of resin solutions with basic pigments may be attributed to a like cause.

(d) *Foreign Impurities.* Adulteration of coumarone resins with coal tar pitch, asphalt, acid resins and similar materials may be detected by treating the sample of resin with concentrated sulphuric acid. The adulterants are more or less attacked by this reagent, whereas coumarone resin is fairly stable. 10 g. of the resin dissolved in 100 ml. of pure benzene is shaken for two minutes with 100 ml. of concentrated sulphuric acid in a separating funnel. Sufficient time is allowed for the mixture to separate, when the acid layer is drawn off and shaken again with a further 50 ml. of benzene. The benzene

solutions are bulked and evaporated in a tared distillation flask, the last traces of benzene being removed by heating in a vacuum, if necessary. The amount of resin which remains represents that portion of the original sample which is unattacked by sulphuric acid. After deduction of the water contents, coumarone resins may contain up to about 20 per cent. of constituents soluble in sulphuric acid. If this limit is exceeded, foreign impurities have probably been added, the precise character of which requires separate investigation. To distinguish coumarone resins from pitches and asphalts, Marcusson recommends the acetone solubility test (p. 290). Other artificial resins, such as bakelites and albertol, may be detected by a benzene solubility test and the soda-lime ignition test (p. 291).

IV. NAPHTHALENE

(a) Properties

Naphthalene comes on the market in various grades, differing in appearance and quality according to the purpose for which it is to be used. Pressed or filtered crude naphthalene is used as a raw material in the manufacture of lamp black, also for preserving raw hides, and as a motor fuel.[1] The pure distilled product is employed in the form of cakes or in a powdered form in the dyestuffs industry, sublimed naphthalene for fumigating purposes, and compressed into tablets, candles, or balls, it is used as a household disinfectant and for the disinfection of urinals, etc. By hydrogenation tetralin and decalin are produced.[2]

(b) Crude Naphthalene

(1) *Properties*

Crude naphthalene is a whitish-grey to reddish-brown oily crystalline mass with a melting-point of about 60°.

(2) *Testing*

Its examination comprises the determinations of crystallizing point, water content, the quantity of phenolic constituents and the amount of matter insoluble in toluole, while a fairly close idea of the oil and/or naphthalene content may be obtained by an extension of the crystallizing point test.

If the sample consists partly or wholly of lumps, the whole must be crushed and passed through an 8-mesh B.S. sieve and thoroughly

[1] Bruhn, *J. Gas Lighting*, 1915, 132, 644; Willis, *Gas J.*, 1918, 141, 65.
[2] Nathan, *Fuel*, 1924, 3, 346.

mixed before any is taken for test. If the sample contains free oil, the whole is melted, care being taken to minimize loss by evaporation, and the portion for any test is poured from the thoroughly mixed liquid direct into the appropriate apparatus.

(a) *Crystallizing point.* The apparatus is shown in Fig. 35, a standard thermometer reading from 65° to 90° C. being used. Small percentages of water affect the crystallizing point of naphthalene appreciably but the lowering of the crystallizing point ceases when a minimum of 2 per cent. of water is present and in the absence of other instructions the presence of that minimum is ensured before test, if necessary by adding 0·5 ml. of water to the inner tube of the crystallizing point apparatus before the sample is introduced.

It may however be desired to carry out the test on the dried sample ; *Standard Methods* describes a drying procedure, based on the maintenance of a desiccating atmosphere saturated with the vapours from commercial naphthalene ; the system prevents the selective extraction of the ingredients other than water of the sample under test.

Finally the crystallizing point may be required on the basis of the material as received—a more common requirement than is sometimes believed by those who are largely or wholly interested in the more important and, especially, export sections of the market. There is then no preliminary treatment of the sample either by drying or by the deliberate addition of water to secure a minimum water content of 2 per cent.

About 40 g. of the material is warmed to 85° C. in a loosely stoppered conical flask, the contents of which are then thoroughly mixed and about 20 g. poured into the warmed inner tube of the apparatus. The assembled apparatus is placed in a water-bath between 6° and 8° C. below the expected crystallizing point. The water-bath is not heated during the subsequent procedure. The rest of the test follows the usual lines of *Standard Methods* for a crystallizing point test.

If the test has been carried out in the presence of at least 2 per cent. of water, the result may be corrected to the dry basis by adding 0·85° C. That result will therefore be the same as if the test was carried out on the material dried according to the requirements of *Standard Methods* in an atmosphere of the vapours from commercial naphthalene. This last technique represents the method prescribed by the United States Customs.[1]

(b) *Water.* This test is carried out substantially in the manner used in *Standard Methods* for other tar products, employing the standard Dean and Stark apparatus ; 100 g. of the sample is used,

[1] United States Customs Memo. T.D. 41515 of 24th April 1926.

being mixed with 100 ml. of solvent naphtha in the flask used in conjunction with the Dean and Stark unit.

(c) *Phenolic Constituents.* The method adopted as standard in the 1938 edition of *Standard Methods* is that of Fox and Gauge [1] and is based on the formation of azo-dyes when alkaline extracts of phenols are mixed with diazotized sulphanilic acid. The colours produced are compared with those of standard solutions.

The stock standard solutions are prepared from an essentially xylenols fraction in aqueous caustic soda solution. The stock solutions keep fairly well, provided they are stored in the dark and well stoppered. The standard solution is prepared therefrom immediately prior to use ; it cannot be regarded as satisfactory for use over more than one day.

In addition, reagents of prescribed strengths are required as follows : sulphanilic acid, sodium nitrite, sulphuric acid, caustic soda and diazotized sulphanilic acid. The last mentioned is prepared five minutes before use by mixing in the correct proportions the sulphanilic acid, sulphuric acid and sodium nitrite solutions in the cold.

For the test, 50 g. of sample is dissolved in 150 ml. of 90's benzole and the solution extracted twice with hot caustic soda solution. The naphthalene solution is washed with hot water and the combined washings boiled for ten to fifteen minutes, cooled to laboratory temperature and filtered. The filtrate, including water washings of the filter paper, are diluted to exactly 500 ml. 5 ml. of this solution is diluted to 50 ml. for test.

2 ml. of the standard tar phenols solution is taken in a 100 ml. British Standard Nessler cylinder, with 5 ml. of the caustic soda solution ; the mixture is diluted to 100 ml. with water and 10 ml. of the diazotized sulphanilic acid solution is added with stirring.

2 ml. of the alkali extract of the sample is treated in exactly the same way in another Nessler cylinder. Comparison of the colours of the two solutions serves to determine the amount of the caustic soda extract of the sample which is necessary to give a colour identical with that given by the 2 ml. of standard tar phenols solution in the first cylinder. The colour matching proceeds until the match is made both as to depth of shade and colour ; it must be completed within ten minutes of the addition of the diazotized sulphanilic acid solution.

It is important that the shades as well as the depths of colour are matched, and the Standard Method prescribes variations which may be made in the making up of the standard tar phenols solution in order to enhance, as required, the yellow or red ingredient of the colour of the standard solution.

There were special reasons why the foregoing method was adopted

[1] *J. Soc. Chem. Ind.*, 1920, **39**, 260 T.

as the standard in 1938. The method for which A. G. Francis was responsible in the 1929 edition of *Standard Methods* was in brief as follows :—

50 g. of a representative sample is dissolved in 100 to 150 ml. of 90's benzole (National Benzole Association Standard Specification No. IV., p. 210) and the solution, filtered if necessary, transferred to a separating funnel, and extracted with two successive quantities, each of 10 ml., of 10 per cent. aqueous sodium hydroxide solution. The solution is then washed with 20 ml. of water, and the three extracts combined in a 500 ml. graduated and previously calibrated flask, and the volume made up to 500 ml. with water. Three stoppered glass flasks (" iodine flasks ") are then taken, into one being introduced 25 ml. of distilled water, into the second 25 ml. of standard cresol solution, and into the third 25 ml. of the prepared soda extract ; the standard cresol solution is made by dissolving 0·35 g. of *ortho*-cresol, 0·40 g. of *meta*-cresol and 0·25 g. of *para*-cresol in 10 ml. of normal aqueous sodium hydroxide solution and diluting to 1 litre with water. A standard solution of potassium bromide-bromate is also prepared by dissolving 20 g. of potassium bromide and 5·6 g. of potassium bromate in exactly 1 litre of water. To the contents of each of the above three flasks is added 25 ml. of the potassium bromide-bromate solution, followed in each case by 5 ml. of concentrated hydrochloric acid. Five minutes is allowed to elapse between the addition of the acid to the separate flasks, thus allowing sufficient time for the subsequent titration of the contents of each flask ; equal time intervals must elapse between the addition of the acid and the titration. 30 ml. of approximately 10 per cent. potassium iodide solution is added to the contents of each flask, the contents well shaken and allowed to stand for five minutes prior to titration with $N/10$ sodium thiosulphate solution.

The percentage of phenolic constituents in the original sample is $\frac{50(a - c)}{w(a - b)}$ where w is the weight in g. of the sample used ; a is the volume in ml. of the thiosulphate solution used in the first flask titration ; b, a like value for the second flask, and c for the third flask, *i.e.* for the sample of naphthalene used.

(d) *Insoluble Matter.* The Standard Method requires 10 g. of sample, which is mixed intimately with 100 ml. of hot 90's toluole in a beaker. When the naphthalene is completely dissolved, the solution is filtered, the method being completed by the washing of the residue on the filter paper, drying to constant weight at a temperature between 95° and 110° C., and weighing, exactly in the manner prescribed for similar determinations on other tar fractions as previously described.

(e) *Oil and/or Naphthalene.* A test, which has been in common use in various laboratories for some time, has been more precisely developed by W. Kirby and appears for the first time in published form in the 1938 edition of *Standard Methods.* The principle is to carry out determinations of one or more " corrected wet crystallizing points." The sample is first tested in accordance with sub-section (a) above in the presence of a minimum of 2 per cent. of water; the correction of 0·85° C. is added to the observed crystallizing point to give the " corrected wet crystallizing point."

If the resulting figure (t_1° C.) is 70° C. or over, the percentage by weight of oil in the sample is $1 \cdot 96\,(80-t_1)$, the percentage of naphthalene in the sample being by inference $1 \cdot 96\,t_1-56 \cdot 8$.

If the result of the foregoing determination on the sample is below 70° C., about 40 g. of pure naphthalene is melted with about 10 g. of the sample, the actual weights of each being accurately known. The " corrected wet crystallizing point " (t_2° C.) of the resulting mixture is determined. The percentage of oil in the sample is $(W+w)d/0 \cdot 51\,w$, where W and w are the weights of pure naphthalene and sample respectively and d is the depression of the crystallizing point of the pure naphthalene and equals $80-t_2$.

(*c*) Pure Naphthalene

(1) *Properties*

Commercially pure naphthalene is used in the dyestuffs industry for the manufacture of such intermediates as mono- and dinitronaphthalene, naphylamine, β-naphthol, nitro- and aminonaphthol and their sulphonic acids and phthalic anhydride. It is a white crystalline mass which volatilizes without residue, melts at 79·6° to 79·8° and boils at 218°; chemically pure naphthalene melts at 80·1°. Its sp. gr. is 1·158 at 18°, and its calorific value is 9620 cals. per g. It is insoluble in water, slightly soluble in hot alcohol, and soluble in petroleum ether and benzene.

(2) *Testing*

Heated with concentrated sulphuric acid it should dissolve to a clear almost colourless solution, at the most slightly pink at 100°, or light-brown at 180°. The solution, on diluting and rendering alkaline with sodium hydroxide solution, should give no smell of pyridine bases, and on adding bromine water and hydrochloric acid to the filtered alkaline extract no clouding should occur due to the formation of bromophenols.

In order to test the stability of its colour on exposure to air and light, the naphthalene is placed on a watch-glass over pure concentrated,

non-fuming nitric acid, the whole being covered with a bell-jar. Under these conditions it should remain colourless for at least one to two hours ; after several hours even the purest naphthalene becomes yellow on the surface owing to the formation of nitro-compounds.

(a) *Crystallizing Point.* The apparatus prescribed in the Standard Method is the same as that used for the determination of the crystallizing point of crude naphthalene (see p. 297), but no question of alternative methods arises and the test is carried out on the sample as received.

(b) *Sulphuric Acid Test.* The principle of the test is to heat the sample with concentrated sulphuric acid and compare the colour developed against standard solutions.

Standard Methods prescribes three standard solutions containing varying quantities of cobaltous nitrate to which sodium sulphide solution is added. The standard solutions must be freshly prepared and for the purpose of the test are carried in large test-tubes matched against each other with special reference to the coloration of the glass.

Into a fourth matched tube, 10 ml. of pure, water-white 98/99 per cent. sulphuric acid is measured and the tube and contents are heated to 80° C. ; 2 g. of the crushed sample is added and, the temperature being maintained at 80° C., the contents of the tube are shaken gently for exactly two minutes. Comparison against the standard solutions follows immediately. The test is a grading one and the report simply states whether the sample gives a colour equal to one or between two of the standards.

(*d*) Detection and Estimation of Naphthalene

White and Ball[1] estimate naphthalene in tar by weighing about 1 g. of tar into a 50 ml. Erlenmeyer flask which is provided with a double-bored cork, one perforation serving as an air inlet, while the other carries a U-tube. The first two-thirds of this tube is filled with quicklime and the remaining space with glass-wool and phosphorus pentoxide. The entire apparatus is contained in an air-bath at a temperature of 70° to 80°. The outlet of the U-tube is connected, outside the air-bath, by means of a short piece of rubber tubing, with a weighed second U-tube immersed in ice water. A current of air is drawn through the apparatus by an aspirator at a velocity of 2 litres per hour, which causes the naphthalene to volatilize and to deposit in the cooled U-tube. The operation is continued until the second U-tube no longer shows an increase in weight. The method is stated to be sufficiently accurate for ordinary purposes, although the naphthalene deposited is not quite pure.

[1] *J. Gas Lighting*, 1904, **88**, 262, 323.

Schläpfer and Flachs[1] review proposed methods of estimating naphthalene in tar and favour that of Glaser as modified by Metzger.[2] Air is passed through the sample contained in a suitable glass-stoppered vessel which is heated in a water-bath in order to volatilize the naphthalene. The naphthalene is absorbed in a picric acid solution. The absorption flask consists of close-fitting concentric cylinders through which the air is forced. Ground glass connections must be used throughout, since loss of naphthalene by diffusion through rubber may be considerable. Excess picric acid is determined by titrating the amount of iodine liberated from a potassium iodide-potassium iodate mixture. Unsaturated compounds in light and heavy tar oils have to be removed by preliminary oxidation with $2N$ potassium permanganate solution in the cold. Bases are extracted with dilute phosphoric acid. The duration of the air current must be timed to avoid entraining compounds of high vapour tension which form picrates.

According to Calcott, English and Downing[3] the percentage of naphthalene in refined or crude naphthalene may be determined by the following method :—

10 g. of refined naphthalene or 12 to 15 g. of crude naphthalene (the quantity taken should contain 8 to 10 g. of pure naphthalene), is weighed into a 500 ml. round-bottomed wide-mouthed flask and 10 ml. of sodium hydroxide solution added; the sodium hydroxide solution is prepared by boiling 5 per cent. sodium hydroxide solution with an excess of refined naphthalene (5 g. of naphthalene per litre), cooling, storing over excess of refined naphthalene, and filtering before use.

Small pieces of filter paper are provided in the flask to prevent the clinging of any tar in the sample to the sides of the flask. The flask and contents are then arranged for steam distillation; the distillate passes in turn through a 500 ml. wash flask, containing 100 ml. of a 10 per cent. solution of sulphuric acid to remove basic impurities, and a Kjeldahl bulb as a trap, and finally into a receiver consisting of a 1 litre flask fitted with a 10 mm. inlet tube reaching almost to the bottom of the flask, and a 10 mm. outlet tube which passes to an auxiliary 500 ml. receiver. The sample flask and wash flask are also directly heated during steam distillation. After twenty minutes the distillation is interrupted and the receiver replaced with a second clean 1 litre receiver. Distillation is complete when nothing but oil separates in the receiver or the receiver fills with an acrid vapour; three receivers are generally required, and the distillation occupies forty-five to sixty minutes. The naphthalene in the receivers is

[1] *Monats-Bull. schweiz. Ver. Gas. Wasserfach*, 1928, **8**, 224, 250, 283, 302; *J. Usines Gaz.*, 1930, **54**, 2, 25, 51.

[2] *Gas- u. Wasserfach*, 1920, **64**, 413.

[3] *Ind. Eng. Chem.*, 1924, **16**, 27.

transferred to a 4-in. (10 cm.) Buchner funnel, washed and filtered; final traces may be removed by dissolving in not more than 10 ml. of 95 per cent. alcohol, recovering by dilution of the alcohol solution with 150 to 200 ml. of water and filtering. The naphthalene is subjected to a thorough washing with distilled water and the well-filtered material transferred to a heavy-walled Pyrex test-tube of 3 cm. internal diameter and 16 cm. in height. 25 ml. of chemically-pure concentrated sulphuric acid and 30 ml. of 20 per cent. oleum are now added, the tube stoppered tightly with a rubber stopper, and the naphthalene sulphonated for one hour at 100°, the tube being carefully shaken every ten minutes. The resulting solution is cooled, diluted with 250 ml. of water, boiled for fifteen to twenty minutes to remove sulphur dioxide and any volatile unsulphonated oil, and made up to 1 litre with water. Aliquot amounts of 25 ml. of this solution are then oxidized with vanadic acid solution; the vanadic acid solution is prepared by dissolving 63 g. of pure ammonium metavanadate (NH_4VO_3) in 220 ml. of distilled water, adding 780 ml. of concentrated sulphuric acid, cooling and storing for use. The oxidized solution is diluted to 500 ml., and 75 ml. of this solution titrated with *N*/10 potassium permanganate solution.

The percentage of naphthalene

$$= (\text{c.c. } KMnO_4 \text{ solution} - \text{blank}) \times \frac{\text{normality of } KMnO_4 \text{ solution} \times 0{\cdot}7117}{\text{weight of sample in aliquot amount of solution taken}}$$

For the quantitative estimation of naphthalene in the form of its yellow crystalline picric acid compound ($C_{10}H_8$, $C_6H_2(NO_2)_3 . OH$, m.p. 149°) the naphthalene must be fairly pure; other aromatic hydrocarbons which form picrates must, of course, be absent. Naphthalene can always be detected in technical products by its great volatility at low temperatures and by its characteristic smell.

V. ANTHRACENE

(a) Properties

Pure anthracene forms white plates with a beautiful blue fluorescence. It melts at 218° and boils at 340° [1]; it is insoluble in water, soluble with difficulty in alcohol, ether, petroleum ether and cold benzene, but readily soluble in boiling benzene and glacial acetic acid. With picric acid a picrate is formed from the benzene solution, and consists of needle-shaped crystals, m.p. 138°. When the benzene

[1] Kirby, *J. Soc. Chem. Ind.*, 1921, 40, 274 T.

solution is placed in sunlight or ultra-violet light the polymer, *p*-anthracene, is formed which melts at 244°, and which is insoluble in benzene. On treatment of anthracene with oxidizing agents anthraquinone is produced. The solubility of anthracene, carbazole and phenanthrene in various solvents is as follows [1] :—

Parts per 100 *parts of solvents at* 15·5°

Solvent.	Anthracene.	Carbazole.	Phenanthrene.
Benzene	1·04	0·72	16·72
Toluene	0·53	0·42	13·80
Solvent naphtha . . .	0·46	0·48	12·52
Pyridine	0·85	12·45	25·54

Anthracene is one of the most important raw materials in the dyestuffs industry, being used for the manufacture of alizarine and a large number of other dyestuffs, for example the indanthrene dyes. Commercial anthracene is never pure, but a crude product of varying degrees of purity. In Germany 40 per cent. crude anthracene (containing 40 to 50 per cent. of anthracene) and 50's, 80's and 95's anthracene are commercial products ; in England an " A " and a " B " quality are distinguished. The former is usually of higher percentage and contains less paraffin and methylanthracene than the " B " quality.

Anthracene residues are also marketed and are used for heating and the production of lampblack. These should not contain more than 4 per cent. of water and 2 per cent. of xylene-insoluble material. Commercially, crude anthracene is a greasy powdery mass with a brownish-green colour and an unpleasant smell. It consists mainly of anthracene, phenanthrene and carbazole ; the minor constituents are high-boiling tar oils, acenaphthene, fluorene, acridine, fluoranthrene, chrysene, methylanthracene, pyrene and other substances of high molecular weight ; naphthalene and solid paraffins are also present.

(*b*) Testing

The technical analysis of crude anthracene includes generally a determination of the content of pure anthracene and tests for such impurities as methylanthracene, paraffins, etc. Occasionally the estimation of phenanthrene and carbazole is of importance.

[1] Clark, *Ind. Eng. Chem.*, 1919, 11, 204.

(1) **Sampling.**—The sampling should be carefully performed according to the standard directions, summarized on p. 126.

(2) **Analysis.**—The anthracene in technical products is exclusively determined as anthraquinone according to the method worked out by E. Luck [1] in the laboratory of the Farbwerke vorm, Meister Lucius und Brüning, which is also termed the "Höchst Anthracene test." *Standard Methods* caters for the market for British made anthracene, and limits the technique standardized to material containing between 35 and 85 per cent. of anthracene. In a supplementary note provision is made for modifications which extend the applicability to lower grades, the examination of anthracenes obtained in the analysis of crude tars in the laboratory being in mind. Further variations in the technique are required for certain specially high grades of anthracene which have become a feature of continental production in recent years. The Standard Method may be summarized as follows :—

1 g. of the sample and 45 ml. of acetic acid are heated in an anthraquinone flask fitted with a reflux air condenser. A slow rate of heating is maintained to keep the contents of the flask gently boiling and over a period of about two hours there is introduced, with approximate uniformity, a solution of 15 g. of chromic acid in 10 ml. of water, to which 10 ml. of acetic acid has been added.

After twelve hours standing, 400 ml. of water is added, the material thoroughly mixed and allowed to stand for a further period. The crude anthraquinone is filtered through a smooth-surfaced filter paper and washed with specified quantities of water, caustic soda solution and boiling water, the final washing processes being used to collect the crystals in the apex of the filter paper cone.

The filter paper is opened up and the anthraquinone transferred to a porcelain dish by means of a fine jet of hot water. Drying on the water-bath and then in an oven at 98° to 100° C. follow, the oven drying being repeated until the weight is constant within 1 mg.

The crude anthraquinone is then treated with oleum for ten minutes at 100° C. and the solution allowed to stand for twelve hours in a water-saturated atmosphere. The crystalline mass is broken up with a glass rod, transferred to a beaker with cold water (200 ml.) and after agitation the whole is allowed to stand for two hours. Filtration with successive water, caustic soda solution and water washes follow on exactly similar lines as are employed in the treatment of the crude anthraquinone. The refined anthraquinone is transferred to the porcelain dish, dried on the water-bath and in the oven to constant weight in the manner already outlined. Finally the dish is heated cautiously over a low flame to volatilize the anthraquinone. The

[1] *Z. anal. Chem.*, 1877, **16**. 81.

percentage by weight of anthracene is 85·6 W, where W is the weight in g. representing the loss by volatilization.

The method is markedly susceptible to variations in the technique, certain experienced workers holding the view that the amounts of water, alkali, etc., used in the washing procedures are particularly critical. Others hold the view that experience rather than critical features of the actual technique is the deciding factor in connection with reliable working ; certainly the handling of the crude and refined anthraquinone, *e.g.* in the transfer from the filter papers to the porcelain dish, demands dexterity, which will increase with experience, for the needle-shaped crystals show a considerable tendency to escape the attention of the operator by their lack of contrast with the material of the filter paper.

The Standardization of Tar Products Tests Committee has reviewed the variations of the test which have appeared in the literature, but has concluded that the original test, when fully particularized and annotated, is better than the various modifications proposed.

Nevertheless, and with special reference to the application of the test to high grade material such as the 95 per cent. anthracene coming from certain sources, a survey of the literature on the subject is valuable.

According to Basset,[1] the anthraquinone produced by Luck's method contains certain impurities which cause the results of the analysis to be slightly too high. Rhodes, Nichols and Morse [2] state that loss may occur if an excess of chromic acid is present (as happens with samples of crude anthracene rich in anthracene), since anthraquinone itself is oxidized by the hot chromic acid-acetic acid mixture. Very little loss occurs in the precipitation of the acetic acid solution by dilution, the separation being almost quantitative, and no loss takes place by sulphonation in the purification by solution in fuming sulphuric acid. A small loss of anthraquinone may occur through volatilization on drying ; at 110° approximately 0·00026 g. per gram per hour volatilizes. Sublimation is complete at 350° in thirty minutes. To eliminate loss due to filtration a hardened filter paper in a Gooch crucible is used in the first filtration, and asbestos, from which the anthraquinone is directly sublimed, in the second filtration. The chief limitation of the Höchst test is the time involved, and several methods, none of which is accepted as standard, have been proposed to reduce this materially. Sielisch [3] employs a method in which the crude anthraquinone is treated with sodium bisulphite solution, the solution filtered to remove impurities, the anthraquinol reoxidized, and the

[1] *Chem. News*, 1896, **73**, 178.
[2] *Ind. Eng. Chem.*, 1925, **17**, 839.
[3] *Z. angew. Chem.*, 1926, **39**, 1248.

anthraquinone, thus precipitated, finally weighed. The procedure is as follows :—

To 1 g. of the sample, dissolved in 45 ml. of boiling acetic acid, a solution of 15 g. of chromic acid in 10 ml. of acetic acid and 10 ml. of water is added at the rate of 1 ml. per minute until the green solution becomes definitely brown. After boiling for a further thirty minutes, the cooled solution is diluted with 400 ml. of ice-cold water, and after fifteen minutes the solution is filtered through a glazed filter. The precipitate is washed with ice-cold water and then with 1 per cent. sodium hydroxide solution, not more than 200 ml. of solution being used. The precipitate is now transferred to a 200 ml. Erlenmeyer flask and warmed with 15 ml. of filtered reducing agent for a few minutes at 60° to 80°. The reducing agent consists of a 10 per cent. sodium hydroxide solution containing 10 per cent. of sodium bisulphite. The red solution obtained is filtered into a warmed suction flask through filter paper contained in a Gooch crucible, which has previously been filled with reducing solution diluted ten times; the crucible must not be allowed to run dry throughout the filtration. The residue is submitted to a second reduction with 5 ml. of reducing agent. The solution is filtered as before and the warm filtrates are oxidized to complete decoloration, with dust-free air or preferably with 5 ml. of concentrated hydrogen peroxide. The precipitated anthraquinone is filtered through a porcelain filter of 7 cm. diameter, washed with hot water until neutral, well drained, dried at 100° and weighed. The determination is completed in three to three and a half hours and the experimental losses are stated not to exceed 1 per cent.

According to Pirak,[1] the results obtained by the original Höchst test are low on account of over-oxidation, and the method of Sielisch also gives low results through incomplete oxidation, a slight amount of chromic acid over that indicated by Sielisch being necessary. Loss by sublimation may be minimized by the use of the filter crucibles advocated by Jacobsohn.[2] Pieters and Koenen [3] first treat the crude anthracene with 4*N* sulphuric acid solution to remove bases, and then extract the phenanthrene in the sample by treatment with toluene, using 100 ml. of toluene per 50 g. of the sample; the anthraquinone is not treated with sulphuric acid or resublimed.

(3) **Detection and Estimation of Impurities.**—1. *Methylanthracene* (m.p. 206° to 207°; b.p. over 360°) is an objectionable impurity of crude anthracene, as it has a bad effect upon the shade of the alizarin produced; anthracene which has been distilled from cannel coal tar or from coal tar pitch is especially liable to contain this impurity. When methylanthracene is present the anthraquinone obtained on analysis does not show the usual characteristic needles, but appears in a more felted condition. Japp and Schultz,[4] who were the first to discover methylanthracene in crude anthracene, described a method for its separation, which depends upon the previous oxidation of the anthracene by dichromate and sulphuric acid, and the subsequent distillation of the residue and

[1] *Z. angew. Chem.*, 1928, **41**, 231.
[2] *Chem. Ztg.*, 1926, **50**, 545.
[3] *Chem. Weekblad*, 1929, **26**, 222.
[4] *Ber.*, 1877, **10**, 1049.

treatment of the distillate with alcohol. Phenanthrene crystallizes out from the alcoholic solution first and the methylanthracene can be obtained from the mother liquor. According to A. G. Perkin,[1] the best method of determining the value of an anthracene containing methylanthracene, in doubtful cases, is its conversion into alizarin.

2. *Phenanthrene* (m.p. 101° ; b.p. 332° [2]) is an important constituent of crude anthracene. Kraemer and Spilker give the following method for its estimation, which, however, gives satisfactory results only when it is present in large quantity :—

1 kg. of crude anthracene is dissolved in 2 kg. of toluene, and allowed to crystallize for about six hours at the ordinary temperature with frequent stirring. The anthracene and carbazole which crystallize out are separated by filtration on the pump and washed with 200 ml. of toluene. After removing the toluene from the combined filtrate and washings by distillation, the residue is fractionally distilled, the portion distilling over between 280° and 340° being crude phenanthrene. This is used for the estimation as follows :—20 g. is boiled for half an hour with 30 g. of picric acid in 300 ml. of dry xylene in a flask with a reflux condenser. After standing for twenty-four hours, with frequent shaking, the crude phenanthrene picrate is filtered on the pump, dried and weighed. The mother liquor is diluted with 50 ml. of xylene and a further 20 g. of crude phenanthrene together with 30 g. of picric acid dissolved in it. The difference between the quantity of crude picrate now obtained, and that of the first crystallization gives the amount dissolved in 250 ml. of cold xylene. From the solubility so obtained, and the weight of the two crystallizations, the united amount of crude picrate derived from 40 g. of crude phenanthrene is ascertained. An aliquot part of this is now crystallized from 95 per cent. alcohol. The pure picrate, which forms brilliant yellowish-red needles, is weighed and to its weight is added an allowance for that remaining in solution in the alcohol (20 g. in 750 g. of 95 per cent. alcohol). 100 parts of pure picrate correspond to 43·7 parts of pure phenanthrene. If the phenanthrene be very impure, 30 g. of the sample and 45 g. of picric acid are used each time. The quantity of xylene added after the first crystallization is in this case increased from 50 to 200 ml. The difference in weight of the two crystallizations then represents the solubility of the crude picrate in 100 ml. of xylene. The picrate which is obtained is tested for purity by decomposing it with ammonia and weighing the hydrocarbon, after removing any acridine which may be present by washing with dilute sulphuric acid.

According to Behrens,[3] phenanthrene is easily detected in crude anthracene by extracting with benzene, evaporating the extract, and treating the latter with a solution of α-dinitrophenanthraquinone in nitrobenzene.

3. *Carbazole* (m.p. 247° ; b.p. 351·5° [4]) *and Phenylnaphthylcarbazole* (m.p. 330° ; b.p. about 450°). These substances exercise like methylanthracene an unfavourable influence on the purification of the anthraquinone. According to Behrens,[5] carbazole is easily

[1] *J. Soc. Dyers and Col.*, 1897, **13**, 81 ; *J. Soc. Chem. Ind.*, 1897, **16**, 563.
[2] Kirby, *J. Soc. Chem. Ind.*, 1921, **40**, 274 T.
[3] *Rec. trav. chim.*, 1902, **21**, 252 ; *J. Soc. Chem. Ind.*, 1902, **21**, 1250.
[4] Kirby, *J. Soc. Chem. Ind.*, 1921, **40**, 274 T.
[5] *Rec. trav. chim.*, 1902, **21**, 252 ; *Chem. Centr.*, 1902, **2**, 540.

detected by extracting with ethyl acetate in the cold, evaporating the solvent on a watch-glass, and warming with a few drops of nitrobenzene and phenanthraquinone; characteristic narrow plates of a coppery lustre are thus obtained.

Carbazole, which has risen in importance commercially, especially as a raw material for the manufacture of potassium cyanide and ferrocyanide, is usually determined quantitatively, according to Kraemer and Spilker, by either of the two following methods. In the first of these the bases are previously extracted from the sample with warm dilute sulphuric acid, and the nitrogen determined in the residue by Kjeldahl's method; from this the amount of carbazole is calculated. The second method depends on the fact, observed by Kraemer and Spilker, that carbazole is converted into its potassium derivative by the action of potassium hydroxide at 220° to 240°. The estimation is carried out as follows:—

40 g. of 80 to 85 per cent. potassium hydroxide is melted in a steel crucible of 80 ml. capacity of the form shown in Fig. 46, the thick wall of which contains a cavity for the reception of a thermometer. The temperature is then kept at 180° to 200°, whilst 20 g. of the crude carbazole or crude anthracene is stirred in. The lid is then placed on the crucible, the temperature kept at 220° to 230° for an hour with frequent shaking, the lid removed, any sublimate returned to the crucible, and the anthracene and other associated compounds driven off at a temperature not exceeding 240°. Two hours suffice for this purpose in the case of carbazole of a high degree of purity, and too much heating is to be avoided. After allowing to cool, the melt is ground up with hot water, made distinctly acid with dilute sulphuric acid, the carbazole collected on a filter, washed, dried and weighed. The product is usually dark coloured and must be purified with toluene, of which 600 to 800 ml. should be used for carbazoles of high percentage. The boiling toluene solution is passed through a folded filter which is afterwards washed with a small measured quantity of toluene. The solution is usually brown, and on standing at 14° to 18° for twelve hours deposits a portion of the carbazole in crystals, which are filtered off on the pump, dried and weighed. The filtrate is measured at 17° and the amount of carbazole in solution calculated according to the solubility table prepared by Becchis,[1] as 0·48 g. per 100 ml. A further allowance for loss of 0·5 g. must be added to the final weight of carbazole obtained. The method does not give very reliable results.
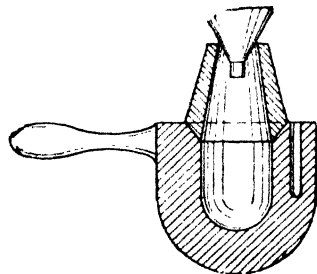
Fig. 46.

[1] *Jahresber. f. Chemie*, 1879, p. 376.

W. Vaubel [1] determines carbazole volumetrically by dissolving it in glacial acetic acid, and adding a standardized potassium bromate solution containing potassium bromide until excess free bromine persists for some time. Each molecule of carbazole absorbs 2 mols. of bromine, although only a monobromo-derivative is formed, in consequence of the oxidation of the imido-group.

Nickels [2] detects phenylnaphthylcarbazole spectroscopically in the benzene solution of crude anthracene by means of two well-defined black bands between lines F and G, and a third which is of still larger wavelength than G.

4. *Solid Paraffins.* Kraemer and Spilker [3] recommend the following procedure :—

10 g. of the very finely ground anthracene is shaken for some time with 70 ml. of ether in a 100 ml. measuring flask, which is then filled up to the 100 ml. mark with ether, mixed well, and allowed to stand till the solid has settled to the bottom. 50 ml. of the clear liquid are then transferred by means of a pipette into a porcelain dish, the ether evaporated, and the residue dried for half an hour at 100°. When cold, the residue is powdered as finely as possible in the dish, well mixed with 8 ml. fuming sulphuric acid (20 per cent. of SO_3), and heated to 100° for three hours, covering the dish with a watch-glass meanwhile and stirring frequently. The contents of the dish are then rinsed into a beaker with 500 ml. of hot water, filtered when cold through a moist filter, and washed with cold water until barium chloride causes no precipitate with the washings. The filter is well drained and rinsed with a little alcohol, after which the paraffin is dissolved out with ether into a weighed porcelain dish. Any traces of paraffin still remaining in the beaker are also washed into the dish with ether. The ethereal solution is evaporated at a gentle heat, dried for half an hour at 105°, and weighed as paraffin.

The Standard Method is based on the removal of aromatic constituents by heating with a considerable excess of sulphuric acid, the unattacked paraffins being separated and weighed.

20 g. of the sample is mixed and heated fairly rapidly to 125° to 127° C. with 290 ml. of 98 per cent. sulphuric acid. The temperature is maintained for half an hour with frequent stirring. The cooled mixture is added to about half a litre of water in a separating funnel, the beaker washed out into the funnel which is then agitated and allowed to stand overnight ; 30 ml. of 60/80 redistilled petroleum ether is used to rinse the beaker and then added to the contents of the separating funnel. The ether layer, on agitation, extracts the paraffins

[1] *Z. angew. Chem.*, 1891, **4**, 748.

[2] *Chem. News*, 1874, **40**, 270 ; 1875, **41**, 52, 95, 117.

[3] Muspratt, *Handbuch der technischen Chemie*, 4th edn., vol. **8**, p. 70.

and after settlement the acid layer is run off and reserved for re-extraction. The petroleum ether layer is run into a smaller funnel and a water wash of the larger funnel is also run into the smaller funnel.

The main bulk of the acid solution is returned to the larger funnel and the extraction process repeated and followed by a further extraction, making three in all.

The contents of the smaller funnel are swirled gently and allowed to stand, when the acid layer is run off. The clear petroleum ether solution is washed successively, ten to fifteen minute separation periods intervening, with specified quantities of caustic soda solution, concentrated sulphuric acid, and distilled water, the last mentioned washing being continued until there is complete freedom from acid.

The petroleum ether solution is then transferred to a weighed beaker, evaporated on the steam-bath and finally dried to constant weight at 100° C.

5. *Hydrocarbons.* The hydrocarbons of coal tar, and hydrocarbons in general, can be quickly identified by the method of Lippmann and Pollak,[1] who make use of the colorations which their solutions in strong sulphuric acid yield on addition of benzal chloride, $C_6H_5.CHCl_2$, in the cold. These are as follows :—

Anthracene	Malachite green.
Naphthalene	Magenta red.
*Benzene	Light yellow.
*Toluene	Light yellow.
*Xylene	Orange.
Phenanthrene	Carmine.
Triphenylmethane	Pale yellow.
Picene	Olive green, after some time.
Diphenylmethane	Brick red.
Stilbene	Bluish green.
*Pseudocumene	Orange red.
*Cymene	Orange.
Pyrene	Emerald green, later deep blue.
Acenaphthene	Dark blue.
Dibenzylanthracene	Yellowish green.
Chrysene	Light yellow, then light green; later dark green.

The hydrocarbons marked * yield the coloration mentioned even without addition of benzal chloride.

[1] *Monatsh.*, 1902, **23**, 670.

VI. PHENOL, CRESOLS AND CARBOLIC ACID PREPARATIONS

(a) Properties

The term "carbolic acid," as used in the chemical trade, is by no means well defined or limited to a definite chemical compound. It not only denotes pure phenol, C_6H_5OH, but also the cresols, their mixtures with phenol, and, further, the crude tar oils containing only a certain percentage of these substances in the crudest state. Fischer [1] gives the phenol content of various tars as follows :—

	Per cent. Phenol.
Ruhr coke-oven tar	0·18
Upper Silesian coke-oven tar	0·41
Saar coke-oven tar	0·59
Gas works tar	0·89

Fischer and Breuer [2] state that low-temperature tars contain about 0·06 per cent. of phenol, a producer low-temperature tar, 0·24 per cent., and that about 1 per cent. of phenol is present, in general, in high-temperature tars. Wiltshire,[3] however, gives a phenol content of low-temperature tar as high as 1·5 per cent. and of a hydrogenated low-temperature tar as 3·8 per cent. Currey [4] gives the approximate composition of vertical retort tar acids as follows :—

Component.	Per cent. by volume on a basis of:		
	Tar acids.	Distillate.	Water-free tar.
Phenol	4	1·2	0·60
Cresols	23	6·9	3·45
Xylenols	22	6·6	3·30
Higher phenol homologues and polycyclic phenols	50	15·0	7·50
Polyhydric phenols (mainly catechol) .	1	0·3	0·15
	100	30·0	15·00

The following are the chief commercial products :—

(1) **Crude Phenol.**—Crude carbolic acids, 60's and 45's, are final products of most English tar works. A few tar works produce distilled

[1] *Ges. Abhandl. Kenntn. Kohle*, 1917, **2**, 184; Fischer and Gröppel, *Z. angew. Chem.*, 1917, **30**, 76, 124.

[2] *Ges. Abhandl. Kenntn. Kohle*, 1918, **3**, 89; *Chem. Zentr.*, 1919, **90**, iv. 1070.

[3] *J. Soc. Chem. Ind.*, 1931, **50**, 125 T.

[4] *Ibid.*, 1923, **42**, 379 T.

carbolic acids, 60's and 45's, but these are essentially intermediate products for the manufacture of crystallized carbolic acid and of cresols. The former may also be used for a like purpose.

British Standard Specifications state the following requirements :—

	Carbolic acids 60's.*			Distilled carbolic acids.	
	A. Crude.	B. Dehydrated crude.	C. Distilled.	60's.	45's.
Water content . .	Not more than 15 per cent.	Not more than 3 per cent.	Not more than 3 per cent.	Not more than 3 per cent.	Not more than 3 per cent.
Specific gravity $S_{15\cdot5°/15\cdot5°}$	Not lower than 1·055	Not lower than 1·055	Not lower than 1·055	Not lower than 1·055	Not lower than 1·055
Crystallizing point .	Not lower than 60° F.	Not lower than 60° F.	Not lower than 60° F.	Not lower than 60° F.	Not lower than 45° F.
Residue on distillation	Not more than 5 per cent.	Not more than 5 per cent.	Not more than 2 per cent.	Not more than 2 per cent.	Not more than 2 per cent.
Neutral oils—					
Grade 1.	Not more than 0·05 per cent.			0·1	0·1
Grade 2.	,, ,, 0·3 ,,			1·0	1·0
Grade 3.	,, ,, 0·6 ,,			...	...
Grade 4.	...			...	...
Pyridine bases—					
Grade 1.	Not more than 0·08 per cent.			0·2	0·2
Grade 2.	,, ,, 0·4 ,,			1·0	1·0
Grade 3.	,, ,, 0·8 ,,			...	...
Grade 4.	...			...	...
Total pyridine and hydrocarbon impurities—					
Grade 1.	Not more than 0·10 per cent.			...	...
Grade 2.	,, ,, 0·5 ,,			...	...
Grade 3.	,, ,, 1·0 ,,			...	...
Grade 4.	,, ,, 2·0 ,,			...	...
Acidity (calculated as H_2SO_4 : not to exceed)—					
Grade 1. . .	0·1	0·2	0·05 .	0·1	0·1
Grade 2. . .	0·2	0·3	0·05 .	...	...
Grade 3. . .	0·2	0·3	0·1 .	...	...
Grade 4. . .	0·2	0·3	0·1 .	...	...
Alkalinity (calculated as sodium hydroxide, NaOH : not to exceed)—					
Grade 1. . .	0·1	0·2	0·05 .	0·1	0·1
Grade 2. . .	0·2	0·3	0·05 .	...	...
Grade 3. . .	0·2	0·3	0·1 .	...	...
Grade 4. . .	0·2	0·3	0·1 .	...	...

* Quoted by permission from *B.S.* 515, 1938.

British Standard Methods are to be employed for the above determinations.

(2) **Phenol (Carbolic Acid Crystals).**—In the pure state, phenol forms a white vitreous translucent crystalline mass, which melts to a strongly refracting colourless liquid possessing a peculiarly harsh, but not unpleasant, aromatic odour, and boiling at 181·7°. The sp. gr. at 15° is 1·066; at the ordinary temperature it is soluble in about 15 parts of water. The values for the melting-point of pure phenol

recorded in the literature cover a very wide range, but the majority lie between 40·5° and 40·8°. Howell[1] gives the melting-point as 40·85°±0·50°, Rhodes and Markley[2] as 40·8°, and Hill and Malisoff[3] as 40·92°.

Products appear on the market with varying melting-points (from 42°, 39° to 40°, and below to 32°), conditioned by the presence of small quantities of moisture and of cresols, which strongly influence this property. The melting-points of phenol containing 0·5, 1·0, 1·5 and 2·0 per cent. of water are respectively 38·8°, 36·9°, 35° and 33·2°.

According to the British Standard Specification,[4] British standard phenol (C_6H_5OH) shall consist of colourless needle-shaped deliquescent crystals or white crystallized masses; or, when specified by the purchaser, can be supplied as a solution of specified strength, the strength to be determined by the Standard Method. 10 g. of the material on mixing with 130 ml. of distilled water must give a complete and clear solution, which must so remain after standing for thirty minutes at 15·5°. The crystallizing point of the material must be between 39·5° and 41°, and its boiling-point about 182°. When heated at 150°±5°, under certain specified conditions, for a period of about two hours, in a gentle stream of clean air, not more than 0·05 per cent. of residue must remain.

According to Mallison,[5] liquid carbolic acid (acidum carbolicum liquefactum; D.A.B.V.) is a mixture of 50 parts of phenol with 5 parts of water. It contains at least 87·8 per cent. of phenol and forms a clear, colourless, or slightly reddish liquid with a sp. gr. of from 1·068 to 1·071.

(3) **Liquid Carbolic Acid, 100 per cent. (Dark).**—An almost black liquid which dissolves in sodium hydroxide solution to either a clear or turbid solution, and boils between 185° and 210°. It consists chiefly of a mixture of the three isomeric cresols, together with a considerable proportion of phenol, xylenols and higher methylated phenols, and is used for crude disinfecting purposes, and for the preparation of the other commercial products.

(4) **Liquid Carbolic Acid, 100 per cent. (Light).**—A yellow or brownish liquid, which darkens on standing, and which boils between somewhat narrower limits of temperature than the above; it behaves similarly towards sodium hydroxide solution. It is used chiefly for pharmaceutical purposes, in the dyestuffs industry and for the manufacture of synthetic resins.

[1] *Proc. Roy. Soc.*, 1932, **137**, A. 418.
[2] *J. Phys. Chem.*, 1921, **25**, 527.
[3] *J. Amer. Chem. Soc.*, 1926, **48**, 918.
[4] Quoted by permission from *B.S.* 523, 1938.
[5] Berl-Lunge, *Chemisch-technische Untersuchungsmethoden*, 1933, vol. iv., p. 315.

(5) **Purified Cresylic Acid or Tricresol.**—A colourless liquid boiling between 185° and 205°, and consisting essentially of the three isomeric cresols, free from hydrocarbons, with traces only of phenol and of higher homologues. The boiling points of the three isomeric cresols are: *o*-Cresol: 191·0°; *m*-cresol: 202·2°; *p*-cresol: 202·0°. The crystallizing points of the three cresols are given variously as follows: *o*-Cresol: 30·45°,[1] 30·75°[2]; *m*-cresol: 11·8°[3]; and *p*-cresol: 33·8°,[4] 36·0°.[5] *Standard Methods* gives the crystallizing points as 31·0°, 12·0° and 34·7°, respectively.

According to Jaeger,[6] the sp. gr. of tricresols at various temperatures are respectively:—22°, 1·035; 50°, 1·015; 100°, 0·974; 150°, 0·925; 180°, 0·889. Schulze[7] gives the proportions of the three isomers in coal tar cresols as follows: *m*-Cresol, about 40 per cent; *o*-cresol, about 35 per cent.; and *p*-cresol, about 25 per cent. Their solubility in water at ordinary temperatures is, according to Gruber[8]:—

Pure *o*-cresol	2·50 volumes per cent.
,, *m*- ,,	0·53 ,, ,,
,, *p*- ,,	1·80 ,, ,,

On the other hand, the anhydrous cresol mixture from coal tar can take up 5 per cent. of water.[9]

For the identification and isolation of the cresols and their homologues, Brückner[10] sulphonates the cresol mixture and then distils it by means of superheated steam, a process formerly applied by Raschig[11] for the recovery of *m*- and *p*-cresols alone. The phenols are heated

Sulphonic acid of	Temperature interval of decomposition.
Phenol	123° to 126°
o- and *p*-cresol	133° ,, 136°
m-cresol	116° ,, 119°
1. 2. 3. xylenol	115° ,, 118°
1. 2. 4. ,,	107° ,, 111°
1. 3. 2. ,,	124° ,, 128°
1. 3. 4. ,,	121° ,, 125°
1. 3. 5. ,,	$>$105°
1. 4. 2. ,,	115° to 118°
o- and *p*-ethyl phenol	$>$105°
m-ethyl phenol	125° to 130°

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1 Dawson and Mountford, *J. Chem. Soc.*, 1918, **113**, 925.
2 Bridgman, *Phys. Rev.*, 1914 (2), **3**, 184.
3 Darzens, *Compt. rend.*, 1931, **192**, 1657.
4 Bramley, *J. Chem. Soc.*, 1916, **109**, 480.
5 Fox and Barker, *J. Soc. Chem. Ind.*, 1918, **37**, 268 T.
6 *Brennstoff-Chem.*, 1923, **4**, 258.
7 *Ber.*, 1887, **20**, 410.
8 *Arch. f. Hyg.*, 1893, **17**, 618.
9 Muter, *Chem. Centr.*, 1890, **1**, 840.
10 *Z. angew. Chem.*, 1928, **41**, 1043, 1062; *Erdöl und Teer*, 1928, **4**, 562, 580, 598
11 G.P. 114975, 1900; *Chem. Zentr.*, 1900, ii., 1141.

with an equal weight of sulphuric acid of sp. gr. 1·84 for a period of three hours at 103°. The product is diluted with several volumes of water and distilled; as concentration progresses the boiling point rises, and the temperature is held at each decomposition interval by regulating the passage of steam through the mixture until no further distillate passes over. For each phenol there is a definite temperature interval at which the sulphonic acid is decomposed. These intervals are given on the previous page.

The fractions obtained by steaming are reduced into their constituents by taking advantage of the different solubilities of the homologous phenolates in 25 per cent. sodium hydroxide solution, and of the sodium salt of the arylglycolic acids of the phenols, in water. The method of Steinkopf and Hopner[1] is modified as follows:—

10 g. of the phenol, in a 100 ml. Erlenmeyer flask, is stirred intimately with 2·5 times the equivalent amount of finely powdered sodium hydroxide until the heat liberated is dissipated. 10 g. of monochloracetic acid is then stirred in, an air condenser is attached at once, and the flask is well shaken; the reaction is completed in about two minutes. The product is dissolved in water, precipitated as free acid by hydrochloric acid, dissolved in ether and extracted as the pure sodium salt with sodium carbonate solution.

Phenol.	Solubility of the sodium phenolate in 25 per cent. sodium hydroxide solution.	Solubility of the sodium salt of the arylglycolic acid of the phenol.
Phenol	Easily soluble	Almost insoluble
o-cresol	" "	Easily soluble
m-cresol	" "	" "
p-cresol	" "	Almost insoluble
1. 2. 3. xylenol	Almost insoluble	" "
1. 2. 4. "	Easily soluble	" "
1. 3. 2. "	" "	" "
1. 3. 4. "	" "	Easily soluble
1. 3. 5. "	Almost insoluble	Almost insoluble
1. 4. 2. "	" "	" "
o-ethyl phenol	Easily soluble	" "
m-ethyl phenol	" "	" "
p-ethyl phenol	" "	" "

o- and *p*-ethyl phenols may be separated by means of the barium salt of their sulphonic acids[2]; 1. 2. 3. xylenol is separated only qualitatively from 1. 4. 2. xylenol by means of the slight solubility of the sulphonic acid of the latter in 50 per cent. sulphuric acid,[3] whilst 1. 3. 2. xylenol, owing to its very weak acidic properties, is not extracted

[1] *J. prakt. Chem.*, 1926, **113**, 137.
[2] Sempotowski, *Ber.*, 1889, **22**, 2662.
[3] Ges. f. Teerverwertung, Duisberg-Meiderich, G.P. 447540.

in considerable quantity by the usual sodium hydroxide treatment, and hence is not likely to be found in samples of tar acids. Brückner found the separation of *m*-cresol, from the other cresols, as the trinitro-derivative according to Raschig's method (p. 329) inapplicable in the presence of either phenol or xylenols owing to the formation of crystalline di- and trinitro-derivatives with the former and resinous products with the latter.

(6) **Technical Cresylic Acids.**—Cresol B.P. is an almost colourless to pale brownish-yellow liquid, becoming darker on keeping or on exposure to light; the odour resembles that of phenol, but is more tarry. It is almost completely soluble in 50 parts of water, freely

	Refined cresylic acid. Graded according to content of cresols and/or xylenols, with or without a percentage of phenol from Grade A, 99·5 per cent. to Grade E, 95 per cent.	Cresylic acid of high orthocresol content.
Water content . .	...	Not more than 0·5 per cent.
Specific gravity, $S_{15\cdot5°/15\cdot5°}$ at 15·5°	...	1·045 to 1·050
Distillation . .	To be agreed between Purchaser and Vendor.	On distillation of 100 ml. at least 90 ml. between 192° and 200° (running-points).
Sulphuretted hydrogen	Not more than a light yellow coloration with lead acetate paper.	
Acids and alkalis .	Neutral to moistened litmus paper.	
Neutral oils and pyridine bases	Not to exceed, according to grade: pyridine bases from 0·15 to 2·0 per cent.; neutral oils from 0·15 to 2·0 per cent.; neutral oils and pyridine bases from 0·25 to 4·0 per cent.; neutral oils, pyridine bases and water from 0·5 to 5·0 per cent.	Not more than 0·1 per cent. neutral oils; not more than 0·1 per cent. pyridine bases.
Orthocresol content .	...	Not less than 45 per cent. of *o*-cresol when tested by Standard Cineole Method.
Colour . . .	The colour is specified in terms of colour units as determined by the use of a Lovibond tintometer.	

soluble in 90 per cent. alcohol, in ether, in chloroform, in glycerin, and in fixed and volatile oils. The sp. gr. at 15·5°/15·5° is 1·035 to 1·050. Not more than 2 per cent. by volume distils below 188° and not less than 80 per cent. by volume between 195° and 205°. In

aqueous solution it is neutral to litmus. The limit for hydrocarbon oil is 0·5 per cent. by volume, and the limit for volatile bases is 0·1 per cent. by volume.[1]

British Standard Specifications are published for refined cresylic acids, Grades A and B,[2] and for cresylic acid of high orthocresol content.[3] The preceding table indicates the respective requirements.

(7) **Orthocresol, Metacresol and Paracresol.**—(a) *British Standard Orthocresol* [4] ($C_6H_4CH_3OH$, 1 : 2) consists of colourless crystals or white crystalline masses which may discolour on keeping or on exposure to light. The crystallizing point is between 30·3° and 31·0° as determined by the Standard Method; the boiling-point

	British Standard cresylic acid (50/55 per cent. metacresol).	British Standard metacresol ($C_6H_4CH_3OH$, 1 : 3).
Specific gravity, $S_{15\cdot5°/15\cdot5°}$ at 15·5°	1·035 to 1·040	1·037 to 1·040
Solubility in sodium hydroxide solution	...	10 ml. mixed with 90 ml. of a sodium hydroxide solution containing 5 g. of sodium hydroxide in 100 g. of solution to give a complete solution remaining clear after standing for thirty minutes at 15·5°.
Residue on evaporation .	...	10 g. heated in a gentle stream of clean air at 150°±5° for about two hours not to show more than 0·05 per cent of residue.
Crystallizing point . .	...	Not lower than 10·5°.
Distillation or boiling-point .	Distillation of 100 ml.: at least 92 ml. between 199° and 204° (running-points).	Boiling-point about 202°.
Water content . . .	Not more than 0·5 per cent.	...
Impurities	Not more than 0·1 per cent. neutral oils, nor 0·1 per cent. pyridine bases; not more than a light yellow coloration with lead acetate paper; neutral to moistened litmus paper.	...

is about 191°. When 10 g. of the material is mixed with 90 ml. of a solution of sodium hydroxide containing 5 g. of sodium hydroxide in 100 g. of solution, the solution should be clear and remain so after standing for thirty minutes at 15·5°. 10 g. of the material

[1] *British Pharmacopœia*, London, 1932 edn., p. 137.

[2] *British Standards Institution, B.S.* 524, 1938.

[3] *Ibid., B.S.* 517, 1938.

[4] *Ibid., B.S.* 522 A, 1938. The data are extracted from the respective specifications by permission of the B.S.I.

heated at 150°±5°, under certain specified conditions, for a period of about two hours in a gentle stream of clean air, should not show more than 0·05 per cent. of residue.

(b) *Metacresol.* British Standard cresylic acid (50/55 per cent. metacresol [1]) is a colourless to pale straw-coloured clear liquid, which may darken to a light brown colour on keeping, or on exposure to light. British Standard metacresol [2] is a colourless to very pale straw-coloured liquid, or solid, which may become slightly brown on keeping or on exposure to light.

The requirements of these two products are indicated on the preceding page.

(c) *Paracresol.* British Standard paracresol ($C_6H_4CH_3OH$—1 : 4) [3] consists of colourless crystals or white crystalline masses, which may discolour on keeping or on exposure to light. The crystallizing point must not be lower than 34·0°, and the boiling-point must be about 202°. The material must pass the tests described in the above table for residue on evaporation and solubility in sodium hydroxide solution.

(8) **Technical Xylenol.**—Technical xylenol is similar in appearance to crude cresol, and the isomeric xylenols are the chief constituents ; it has a boiling range of 200° to 220° and gives a clear solution with sodium hydroxide solution.

(9) **Carbolic Acid Preparations.**—Carbolic acid preparations include saprocarbol, lysol, creolin, carbolic soap, and similar products. The Liquor Cresolis Saponatus of the British Pharmacopœia is required to contain 50 per cent. of cresols (limits 47 to 53 per cent.). Most lysols on the market also claim to contain this quantity, but there are brands of lower strength, sometimes sold in a manner constituting a contravention of the law.

(*b*) Detection of Phenol

The most reliable qualitative test for phenol is Landolt's [4] well-known reaction with bromine water, which gives a white precipitate of tribromophenol. With 1 part in 44,000 an immediate and very distinct turbidity is obtained, whilst with 1 part in 60,000 it is distinct after standing for twenty-four hours. Other phenols also give precipitates of bromophenols when treated with bromine water, but they can be distinguished from phenol itself by the differing melting-point of the product. Tribromophenol melts at 94° and crystallizes from dilute alcohol in long, fine, hair-like needles. Thymol yields a turbidity

[1] *British Standards Institution, B.S.* 521, 1938.

[2] *Ibid., B.S.* 522 B, 1938.

[3] *Ibid., B.S.* 522 C, 1938. The data are extracted from the respective specifications by permission of the B.S.I.

[4] *Ber.*, 1871, **4**, 770.

immediately at a dilution of 1 in 60,000, and is thus even more sensitive to this test than phenol. Aniline and similar bases are also precipitated by bromine water, but can easily be distinguished from phenol by filtering and washing the precipitate and warming it gently in a test-tube with water and a little sodium amalgam. If the liquid is then poured into a small dish and acidified with sulphuric acid, the characteristic smell of phenol becomes apparent if phenol was originally present.

Liebermann's reaction is also reliable.[1] The phenol, which has been liquefied with a trace of water, is treated with concentrated sulphuric acid containing 6 per cent. of sodium or potassium nitrite, when a brown coloration is obtained which changes to green and blue successively, owing to the formation of Liebermann's phenol dyestuffs.

A very delicate test for phenol is that obtained with Millon's reagent, the limit of sensitiveness being 1 in 200,000. This reagent consists of mercurous nitrate solution containing a little nitrous acid, and was first recommended as a test for phenol by Plugge.[2] Vaubel[3] studied the reaction in detail and came to the following conclusions in regard to its application: The reagent, as prepared by dissolving 1 part of mercury in 1 part of cold fuming nitric acid or 1 part of nitric acid of sp. gr. 1·4, warming towards the end of the reaction, and diluting with 2 parts of distilled water, contains a little nitrous acid, but mainly mercurous nitrate and nitric oxide, of which, perhaps, a little is converted into nitrogen dioxide by the oxygen of the air. These gases are absolutely essential for the reaction, and much warming must therefore be avoided during the preparation of the reagent as they are easily driven off by heat.

Di-*o*- and di-*m*-substituted phenols do not yield the reaction; among the naphthols, β-naphthol alone gives a similar product, α-naphthol and derivatives giving nitroso-compounds.

Almen[4] adds 5 to 10 drops of Millon's reagent to 20 ml. of the solution to be tested, boils and removes the yellowish-red turbidity of basic salts, which is usually formed, by careful addition of nitric acid. The red coloration thus produced becomes still more intense after a short time. The same reaction is given by salicylic acid.

In order to detect phenol in presence of salicylic acid, ammonia and sodium hypochlorite are added to the liquid. In this way 1 part of phenol in 50,000 can be detected by the blue coloration, which, however, at this dilution requires twenty-four hours' standing for its appearance.

[1] *Ber.*, 1874, **7**, 247.
[2] *Z. anal. Chem.*, 1872, **11**, 173.
[3] *Ibid.*, 1900, **13**, 1125.
[4] *Pharm. J.*, 1887, **7**, 812.

Chapin [1] employs Millon's reagent for the colorimetric determination of phenol in the presence of the other phenols and gives the following directions for its preparation :—

2 ml. of mercury is measured from a small burette into a 100 ml. Erlenmeyer flask, and 20 ml. of pure concentrated nitric acid is added ; the mercury dissolves in about fifteen minutes. The solution is diluted with 35 ml. of water and, if a basic salt separates, nitric acid is added drop by drop until all is dissolved. 10 per cent. sodium hydroxide solution is then added by drops with thorough mixing, until the somewhat curdy precipitate first formed no longer redissolves, but disperses to an evidently permanent turbidity. Exactly 5 ml. of dilute nitric acid containing 0·2 of its volume of pure concentrated nitric acid is now added and the solution well mixed ; the same Millon's preparation should be used for the sample and standard and the preparation must be freshly made.

In making a test, 4 mg. of the phenol or mixture of phenols in nearly neutral aqueous solution is placed in a 20 mm. test-tube and 5 ml. of the Millon's reagent added and the contents well mixed. The test-tube is now heated in a boiling water bath for exactly thirty minutes ; after fifteen minutes boiling the original red colour from other phenols may not be entirely discharged, nor will the colour from phenol have been fully developed. The test-tube is then transferred to a bath of cold water in which it is allowed to remain for ten minutes. The contents are now acidified with 5 ml. of dilute nitric acid containing 0·2 of its volume of pure concentrated nitric acid, free from oxides of nitrogen,[2] and after brief mixing brought up to a total volume of 25 ml. with water and thoroughly mixed. If phenol only is present the solution is perfectly clear ; most other phenols yield sediments, comparable in colour to the solutions, which may be removed after standing about ten minutes.

The following table (p. 322) gives the colours obtained with various phenolic bodies.

Chapin's method, on a strictly quantitative basis, has been adopted as the Standard Method for use in certain circumstances, and is dealt with later (p. 340).

According to Wilkie,[3] much the most sensitive test for phenol (also given by salicylic acid) is the formation of the very voluminous tri-iodophenol. This is carried out by adding to the solution *N*/10 iodine and sodium carbonate and, after five minutes, acidifying, when the tri-iodophenol is precipitated. Less than 1 part of phenol per million can be thus detected, whilst 4 parts per million give an immediate indication.

[1] *United States Department of Agriculture Bulletin*, No. 1308, 22nd November 1924.

[2] Blown with air till colourless, if necessary.

[3] *J. Soc. Chem. Ind.*, 1911, **30**, 402.

Carlette[1] states that small quantities of phenol in salicylic acid, or of phenates in salts of this acid, may be identified by stirring together 0·25 g. with 5 ml. of distilled water in a test-tube, adding 2 drops of a 2 per cent. alcoholic furfural solution, and then pouring 2 or 3 ml. of concentrated sulphuric acid down the side of the tube so that it

Phenol.	Colour of solution.	Colour after adding formaldehyde.
Phenol	Deep red	Strong yellow
o-cresol	Faintly orange	Greenish-yellow
m-cresol	Strong yellow	Very slightly paler
p-cresol	Greenish-yellow	No change
o-xylenol	Faintly orange	Greenish-yellow
p-xylenol	Greenish-yellow	No change
Thymol	Faint greenish-yellow	,,
Resorcinol	Greenish-yellow	,,
Pyrogallol	Colourless	,,
Guaiacol	Faintly orange	Greenish-yellow
α-naphthol	Greenish-yellow	No change
β-naphthol	Strong brown	,,
Salicylic acid	Deep red	Strong yellow

forms a layer on the bottom. A yellow ring forms at the contact zone, above which, according to the quantity of phenol present, a deep blue ring appears, even if the contained phenol only amounts to 0·00005 g.

Endemann[2] evaporates a solution of formaldehyde (formalin) with phenol almost to dryness, and adds a dehydrating agent such as concentrated sulphuric acid ; coloured products are obtained, probably of the triphenylmethane series, which vary in colour with the particular phenol present.

Herzog[3] recommends diphenylcarbamic chloride, $(C_6H_5)_2N \cdot COCl$, in pyridine solution as a reagent for phenols ; it produces the corresponding phenolic diphenylcarbamate.

Runge's well-known ferric chloride reaction is given by many other substances besides phenol.[4]

Escaich[5] describes a modification of the quinone-imide test for phenol, according to which 10 to 15 ml. of the solution to be tested is treated with 5 to 10 drops of ammonia, 0·05 to 0·1 g. of sodium persulphate and 4 to 5 drops of *N*/10 silver nitrate solution. A green colour is produced which rapidly intensifies and changes to blue for concentrations of phenol exceeding 0·05 g. per litre, and which becomes yellow for lower concentrations. 10 ml. of a phenol-containing solution may be treated with 1 drop of 10 per cent. sodium nitrite

[1] *Chem. Centr.*, 1907, **II**, 427. [2] *Z. anal. Chem.*, 1901, **40**, 667. [3] *Ber.*, 1907, **40**, 1831.
[4] *Cf.* Hess, *Annalen*, 1876, **182**, 161 ; also Raschig, *Z. angew. Chem.*, 1907, **20**, 2065.
[5] *J. Pharm. Chim.*, 1920, **22**, 138.

solution and the whole poured on the surface of concentrated sulphuric acid ; a coloured zone develops at the point of contact of the two liquids, the upper part of the zone being red and the lower green.[1] According to Moir,[2] the solution to be tested is treated with 5 ml. of *p*-nitraniline hydrochloride solution (*p*-nitraniline 1·5 g. ; hydrochloric acid 40 ml. ; water 500 ml.), decolorized previously by the addition of sodium nitrite solution. If much phenol is present an orange-coloured precipitate is formed which changes to salmon-pink to ruby-red on rendering the solution alkaline with sodium hydroxide solution dependent on the quantity of phenol present.

Ware[3] recommends the following test for the detection of phenol in cresols :—

The sample of cresol is shaken with *N*/10 potassium hydroxide solution and, after separation, the upper layer is removed, shaken with ether, acidified after removal of the ether, and finally again extracted with ether. The residue remaining after evaporation of the second ether extract is acidified and stirred with a mixture of sodium nitrite and sodium nitrate. The development of a crimson colour denotes the presence of phenol.

Ware[4] also describes distinguishing tests for carbolic acid, the cresols and certain other phenols :—

1 drop of the solution to be tested is dissolved in 10 ml. of hydrochloric acid, 0·5 g. of a mixture of sodium nitrite (1 part), potassium or sodium nitrate (1 part), and dehydrated sodium sulphate (2 parts) is added and the whole is stirred. After two to five minutes the colour (*a*) is noted and then 1 ml. of the acid mixture is poured into excess of 10 per cent. ammonia solution and any colour change (*b*) noted. Carbolic acid gives a rich crimson colour (*a*) changing to purple on the addition of 1 to 2 drops of 38 per cent. formaldehyde, which, on pouring into ammonia solution, becomes deep blue. *o*-cresol gives a dichroic solution with green predominating, changing with formaldehyde to blue and with ammonia to olive-green. *m*- and *p*-cresols and Cresol B.P. fail to give any distinctive results, and *p*-cresol inhibits the reaction with carbolic acid or *o*-cresol. *β*-naphthol and *α*-naphthol give for (*a*) a crimson-purple and violet-purple respectively, and for (*b*) the colour is destroyed. Thymol gives (*a*) a green and (*b*) a yellow colour ; Cresol B.P. gives similar results to *m*-cresol and Creosote B.P. to guaiacol.

(*c*) Examination of Crude Commercial Products

Crude commercial products such as crude phenol and crude carbolic acid should be examined according to the methods described

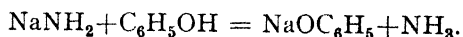
[1] Rodillon, *J. Pharm. Chim.*, 1921, **23**, 136.
[2] *J. S. Afr. Chem. Inst.*, 1922, 5, 8.
[3] *Pharm. J.*, 1927, **118**, 775.
[4] *Analyst*, 1927, **52**, 335.

on p. 198 for the examination of crude tar acids. Commonly, in the case of crude carbolic acid, both the works and the trade employ the following method for determining the percentage of phenols :—

10 volumes of the crude carbolic acid are shaken for a considerable time with 90 volumes of sodium hydroxide solution of sp. gr. 1·079, and after settling completely, the remaining volume of oil is calculated as non-phenols. The sodium phenate solution is separated from the oil, acidified with hydrochloric acid, the phenols salted out with common salt, and the volume of crude moist phenols read off. The volumes of phenols and non-phenols thus found should together be approximately equal to the original volume of the sample.

The method is open to objection as the solution of sodium phenate is capable of dissolving considerable quantities of tar hydrocarbons and bases, the former being thus reckoned as phenols, whilst the latter, which remain in solution on acidification, are not included in the non-phenols or in the phenols. The result would be more exact if before acidifying the sodium phenate solution the bases were distilled off in a current of steam, collected and added to the non-phenols. The increase in volume of the separated phenols due to dissolved water approximately compensates for the amount of phenols remaining dissolved in the hydrochloric acid.

Schryver [1] describes a method which consists in the treatment of the phenol in benzene solution with sodamide and estimation of the ammonia evolved, by the usual volumetric methods :—

$$NaNH_2+C_6H_5OH = NaOC_6H_5+NH_3.$$

About 1 g. of finely powdered sodamide is washed two or three times by decantation with small quantities of thiophen-free benzene and introduced into a 200 ml. wide-mouthed flask, connected with an inverted condenser. 50 to 60 ml. of thiophen-free benzene is added, and the mixture boiled on the water-bath for ten minutes, dry air (free from CO_2) being aspirated meanwhile through the apparatus to remove entirely any traces of ammonia. 20 ml. of a normal solution of sulphuric acid is then introduced into a suitable absorption vessel connected to the outlet to the flask through the condenser, and the phenol, dissolved in about six times its volume of thiophen-free benzene, introduced into the mixture, drop by drop, the contents of the flask being maintained at the boil. When all the phenol has been added, air is again aspirated through the apparatus until all the ammonia is absorbed. The excess of sulphuric acid is determined by titration with normal sodium carbonate solution. The benzene holds ammonia somewhat pertinaciously, and one and one-quarter hours are generally required for the complete expulsion

[1] *J. Soc. Chem. Ind.*, 1899, **18**, 553.

of the latter. Enough phenol is generally employed to require 10 to 17 ml. of normal sulphuric acid solution for the complete neutralization of the ammonia evolved.

Unfortunately the difficulties encountered under ordinary laboratory conditions render the process difficult of application.[1]

(*d*) Examination of Refined Products

The examination of refined tar acids generally includes a distillation assay, the determination of the crystallizing point, the test for clear solubility in water, the colour, the odour, the test for sulphuretted hydrogen, and a determination of neutral oils and pyridine bases according to the method described previously (p. 198). The residue on evaporation of certain products is determined.

1. **The Distillation Test** for refined carbolic and cresylic acids is that described on p. 198 as applicable to the crude acid.

2. **Crystallizing Point.** — The test for crystallizing point in connection with a refined acid is carried out in the standard apparatus (Fig. 35), the thermometer depending on the material under test; that for crystallizing points up to 18° C. has a range of −10° to +20° C.; for crystallizing points above 18° C. and up to 42° C. the standard thermometer has a range of 15° to 45° C.; and one having a range of 39·5° to 70·5° C. is used for crystallizing points above 42° and up to 70° C. The thermometer in each case is graduated to 0·1 of a degree and of course each is required to comply with the relevant full specification given in *Standard Methods*.

About 20 g. of sample is used and a preliminary rapid cooling of the molten mixture is carried out to determine the approximate crystallizing point. Gentle warming follows until all but the last traces of crystal are melted, when the apparatus is assembled and placed in a bath between 6° and 8° C. below the expected crystallizing point. The remainder of the method follows the usual lines for the determination of crystallizing points in *Standard Methods* (see for example p. 227).

3. **Solubility in Water.**—The British market is only interested in the solubility of phenol in water and the Standard Method is limited to tests on that material only. 5 g. of the sample is taken in a weighed conical flask, undue exposure to the atmosphere being avoided. About 50 ml. of distilled water at 15·5° C. is added and the flask gently shaken, the temperature being maintained at 15·5° C. throughout the test. Further small quantities of the distilled water are added with intermediate shaking until all oily globules have just disappeared; $(W-5)/5$ represents the number of parts of water

[1] Fox and Barker, *J. Soc. Chem. Ind.*, 1917, **36**, 842.

required to dissolve one part of sample, W being the weight of the contents of the flask at the end of the test.

4. **Colour and Odour.**—Phenol (including the synthetic product) frequently shows a pink colour. A penetrating odour of sulphur compounds or of other tar products should not be noticeable in good samples. The colour of cresylic acids is a feature of specifications for the refined material and a Standard Method is provided. Cresylic acids vary in tint from yellow to red shades while the colour darkens on keeping or on exposure to light. The Standard Method describes four colours—white, very pale, pale and medium dark—and in respect of the second, third and fourth recognizes a red and a yellow shade for each. Standard solutions representing the limit of depth of colour and shade in each case are detailed with their respective compositions, based on solutions of one or more of the following: cobalt sulphate, potassium dichromate, copper sulphate and potassium ferricyanide.

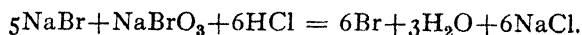
Comparisons are made between the sample and the standard solutions in standard Nessler cylinders (50 ml. capacity); material darker in colour than the appropriate shade of the medium dark solutions is reported as dark or Grade 5.

The Tintometer Limited has developed a comparator in which comparisons are facilitated, the standard solutions being replaced by a disc carrying slides matched in colour with the standards.

5. **Sulphuretted Hydrogen.**—20 ml. of the sample is measured into a 100 ml. Erlenmeyer flask, over the mouth of which is placed a piece of filter paper just previously moistened with a 10 per cent. aqueous solution of lead acetate. The flask is placed on a boiling water bath, and after a period of five minutes the paper is examined for coloration.

6. **Quantitative Estimations of Phenol.**—Phenol may be quantitatively determined either by the method of Koppeschaar,[1] which depends on Landolt's tribromophenol reaction; or by Messinger and Vortmann's method.[2] Both methods yield equally accurate results.

(a) *Koppeschaar's Method.* Instead of bromine water, Koppeschaar uses a solution of sodium bromide and bromate, which evolves bromine with hydrochloric acid in accordance with the equation :—

$$5NaBr + NaBrO_3 + 6HCl = 6Br + 3H_2O + 6NaCl.$$

The following stock solutions are required :—(*a*) A solution of sodium thiosulphate equivalent to a solution containing 5 g. of iodine per litre. (*b*) A solution containing 125 g. of potassium iodide per litre. (*c*) A solution of $5NaBr + NaBrO_3$, of such strength that 50 ml. when mixed with 10 ml. of the potassium iodide solution, 5 ml. of

[1] *Z. anal. Chem.*, 1876, **15**, 233.
[2] *Ber.*, 1890, **23**, 2753.

strong hydrochloric acid, and 100 ml. of water, will require for decolorization 86 to 95 ml. of the sodium thiosulphate solution. This solution is prepared by treating fairly pure sodium hydroxide solution with excess of bromine, evaporating to dryness, and powdering the residue; 9 g. of this residue is dissolved in 100 ml. of water and diluted to the correct strength after titration.

To carry out the estimation, 4 g. of the sample (or more of preparations containing comparatively little phenol) is dissolved in a litre of water. 25 ml. of this solution is placed in a stoppered flask of about 250 ml. capacity, 100 ml. of the bromide-bromate solution added, followed by 5 ml. of concentrated hydrochloric acid, the flask closed, the contents well shaken and allowed to stand for fifteen minutes. 10 ml. of the potassium iodide solution is then added, and the whole again shaken. The liberated iodine is then titrated with the sodium thiosulphate solution, adding starch towards the end of the operation. If the solutions are of exactly standard strength and the operations are carried out precisely as prescribed, the percentage of phenol in the sample is given by the formula :—

$$(2a-b) \times 0{\cdot}61753,$$

where a is the number of ml. of sodium thiosulphate solution required by the bromide-bromate mixture used, and b the number of ml. required by the final excess of bromine.

In preparations containing little phenol, a multiple of 4 g. of the sample may be taken for the estimation, but in no case should 25 ml. of the filtered liquid used for the titration contain more than 0·1 g. of pure phenol.

Beckurts[1] recommends the following modification of Koppeschaar's method, using the standard solutions proposed by Seubert.[2] These consist of $N/20$ potassium bromide solution (containing 5·939 g. KBr per litre), N/100 potassium bromate solution (containing 1·666 g. per litre), $N/10$ sodium thiosulphate solution, and potassium iodide solution containing 125 g. per litre. For the estimation, 25 to 30 ml. of the phenol solution of 0·1 per cent. strength is shaken in a stoppered flask with 50 ml. of each of the standard bromide and bromate solutions together with 5 ml. of strong sulphuric acid. After ten to fifteen minutes, 10 ml. of the potassium iodide solution is added, and the liberated iodine titrated with $N/10$ thiosulphate solution, each millilitre of which is equal to 0·008 g. Br or 0·00156 g. of phenol.

(b) *Messinger and Vortmann's Method.* When iodine acts on an alkaline phenol solution, six atoms of iodine are used up by each molecule of phenol. The excess of iodine is then titrated back after acidifying with dilute sulphuric acid. For the determination, from

[1] *Arch. Pharm.*, 1886, **24**, 561. [2] *Ibid.*, 1881, **18**, 321.

2 to 3 g. of the phenol is dissolved in sodium hydroxide free from nitrite, at least 3 molecules of sodium hydroxide being used for each molecule of phenol. The solution is diluted to 250 or 500 ml., and 5 or 10 ml. of this liquid is warmed in a small flask to 60°. Standard iodine solution is then added, with shaking, until the liquid is of a deep yellow colour, and a red precipitate is formed. The mixture is cooled, acidified with dilute sulphuric acid, diluted to 250 or 500 ml., filtered, and 100 ml. of the filtrate titrated with *N*/10 sodium thiosulphate solution. The amount of iodine used up, multiplied by 0·12356, gives the amount of phenol. This method is accurate, but like Koppeschaar's method, can be employed only for solutions of pure phenol, and not in the presence of homologues or of hydroxy-acids.

This method has been subjected to a careful study by Wilkie,[1] who has worked out the following improved procedure :—

To the dilute phenol solution are added equal volumes of *N*/10 iodine and sodium carbonate. After five minutes, excess of sulphuric acid is added, and the residual iodine titrated with *N*/10 sodium thiosulphate and starch. Should too little iodine have been added, this is indicated by pronounced fading of the brown colour due to the iodine, and in extreme cases by precipitation of tri-iodophenol ; in such circumstances more iodine and sodium carbonate are to be added, and the determination completed in the usual manner, after five minutes' standing. Generally not more than half the added iodine should enter into reaction. The determination is most conveniently carried out in stoppered bottles.

The whole operation is performed in the cold. The primary product of the reaction is tri-iodophenol, but if the reaction mixture is allowed to proceed for twenty minutes before acidification, a secondary reaction takes place with production of the red coloured tetra-iododiquinone : $2C_6H_2I_3(OH) = C_{12}H_4I_4O_2+2HI$.

Telle[2] uses a standardized sodium hypochlorite solution, made by diluting 35 ml. of the solution, as ordinarily sold, to 1 litre. This is added to an acid solution of potassium bromide and this solution used instead of the Koppeschaar or Seubert's reagent. Bader[3] has proposed an alkalimetric method for the estimation of phenol, and Tocher[4] a volumetric permanganate method (*cf.* also Skirrow[5]).

Standard Methods uses in principle Koppeschaar's method for the determination of phenol in liquefied phenol. 0·1 *N*. bromide-bromate solution and approximately 0·1 *N*. sodium thiosulphate solution are used, the latter being standardized against the former as follows :— 30 ml. of the bromide-bromate solution is run into a stoppered narrow-

[1] *J. Soc. Chem. Ind.*, 1911, **30**, 398.
[2] *J. Pharm. Chim.*, 1901, **14** (7), 289.
[3] *Z. anal. Chem.*, 1892, **31**, 58.
[4] *Pharm. J.*, 1901, **66**, 360.
[5] *Ind. Eng. Chem.*, 1917, **9**, 1102.

necked bottle and 5 ml. of 20 per cent. potassium iodide solution is added, followed by 5 ml. of concentrated hydrochloric acid. The bottle is immediately stoppered and thoroughly shaken. The liberated iodine is titrated with the sodium thiosulphate solution, starch solution being added when the contents of the bottle are faintly yellow. The factor (n) of the thiosulphate solution is V/v where V and v are the volumes respectively of the bromide-bromate solution and thiosulphate solution used.

About 1·5 g. of the sample is weighed accurately and dissolved in water to 1000 ml.; 25 ml. of the solution is placed in a stoppered narrow-necked bottle, followed by 30 ml. of the bromide-bromate solution and 5 ml. of concentrated hydrochloric acid. The bottle is immediately stoppered, shaken repeatedly over a period of half an hour and allowed to stand for fifteen minutes. 5 ml. of 20 per cent. potassium iodide solution is added, the bottle shaken thoroughly and the contents titrated as before. Traces of iodine on the stopper must be washed into the bottle before the titration is completed. The percentage phenol content is $0{\cdot}272\ (V-nv)/W$ where V and v are the volumes of bromide-bromate solution and sodium thiosulphate solution used, n is the factor obtained previously and W is the weight of sample taken.

7. **Cresol.**—The value of commercial cresol (cresylic acid) is dependent for some purposes on the proportion of *m*-cresol which is present. Various methods of determining the *m*-cresol in these mixtures have been proposed.

The method of Raschig[1] depends on the fact that on treating *m*-cresol with excess of nitric acid at 100°, it is quantitatively converted into trinitrometacresol, whilst its isomers are completely oxidized, forming oxalic acid. The Raschig technique as developed in connection with *Standard Methods* has been the subject of extended investigation and the Standard Method must be consulted and followed precisely if reliable results are to be expected. The method is outlined below and is applicable to mixtures containing (*a*) not more than 5 per cent. of phenol or 10 per cent. of xylenols; (*b*) not less than 45 per cent. or more than 80 per cent. of metacresol; and (*c*) not more than 1 per cent. of water. Samples not complying with these requirements may be brought into line by the addition of appropriate ortho-metacresol mixtures, the addition of pure orthocresol or pure metacresol, or by drying in the prescribed manner, respectively.

Exactly 10 g. of the sample and 15 ml. of 96·0 ±0·2 per cent. sulphuric acid are mixed in a conical flask, the flask then being maintained at 100° C. for an hour, when its contents are transferred

[1] *Z. angew. Chem.*, 1900, **31**, 759; *cf.* Fox and Barker, *J. Soc. Chem. Ind.*, 1920, **39** 169 T.

to a 1000 ml. flask. The liquid sulphonic acid is distributed on the walls of the flask by rotating in water at 20° C. Nitric acid containing $63{\cdot}25 \pm 1{\cdot}00$ per cent. is made up and 90 ml. is taken in a cylinder at 20° C. About 20 ml. is transferred to the flask originally used, shaken therein and returned to the cylinder, this washing of the first flask being repeated until all the sulphonic acid therein is transferred to the cylinder.

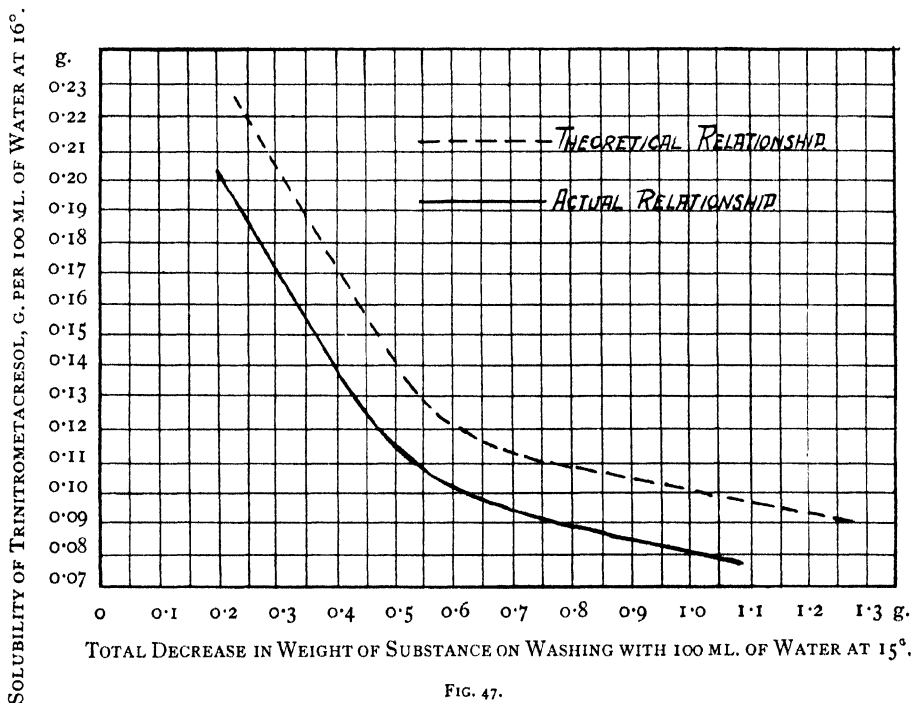
The contents of the cylinder are transferred cautiously to the litre flask and that flask immediately shaken at arm's length until solution is complete and brown fumes are copiously evolved. The flask is then allowed to stand for twenty minutes without undue cooling, after which the contents are poured into a porcelain dish containing 40 ml. of water at about 20° C. A further 40 ml. of water at the same temperature is used in successive small quantities to rinse the flask into the porcelain dish. After standing for two hours, the solid mass which forms in the dish is reduced to a uniform coarse powder and transferred to a Jena glass filtering crucible, No. 2G3. Distilled water at about 20° C. is used in a fine stream to transfer any remaining powder from the dish to the crucible, 100 ml. being used in all, in such portions that on transference, the crucible is only half filled. When all the solid has been transferred, any of the 100 ml. of wash water remaining is used to wash the contents of the crucible.

The dish and contents (trinitrometacresol) are dried to constant weight at 95° to 100° C. The percentage content of metacresol is $10\,W/1{\cdot}75$ where W is the weight in grams of trinitrometacresol.

Raschig states that the presence of even 10 per cent. of phenol does not diminish the accuracy, as the picric acid which is formed remains in the solution ; but the method must not be applied to mixtures containing very large amounts of phenol, which, however, do not often occur in practice. In such samples the presence of phenol is detected by the boiling point, and also by the fact that the nitro-compound does not remain solid in the oven at 95° to 100°, but melts or, at any rate, forms a soft paste. Xylenols, which sometimes occur in commercial cresols, behave in a similar manner ; the nitro-compound either liquefies when warm or refuses to set in the cold. But a cresol which distils for the most part between 190° and 200°, and therefore contains scarcely any phenol or xylenol, always yields a pale yellow crystalline mass, the weight of which when divided by 1·75 gives the weight of *m*-cresol in the mixture, the error being within 1 per cent. If the compound melts at or below 95° to 100°, the test must be discarded, and repeated with the addition of pure *m*-cresol to the original sample. The amount of nitric acid used is considerably more than is needed for the nitration and oxidation, and good results can be obtained with average cresols containing 35 to 60 per cent. *m*-cresol,

when only 70 ml. of nitric acid is used ; but if this is done the reaction often occurs so suddenly that there is scarcely time to mix the sulphonic acid with the nitric acid and place the flask on one side ; explosions have even been known to occur under these conditions. The recognized quantity of 90 ml. of acid is therefore adhered to.

According to Qvist,[1] if the material contains a high percentage of *m*-cresol, correct results are obtained only if a mixture of 60 per cent. of fuming and 40 per cent. of ordinary strong nitric acid is used, and the factor for dividing the weight of the nitro-compound is increased from Raschig's original figure of 1·74 to 1·786. If the crude cresol contains much phenol, a mixture of picric acid and trinitro-*m*-cresol

FIG. 47.

is obtained on nitrating ; careful washing with cold water removes all the picric acid together with a small amount of the cresol compound, a correction for which is made by measuring the washings and referring to a solubility curve given (Fig. 47). The filtrate from the mixed nitro-products is diluted to 230 ml. and distilled in steam until 250 ml. of distillate have collected. The residual solution in the distilling flask is diluted to 250 ml. and extracted twice with 50 ml. of toluene ; the toluene solution is then dried by filtration through thick filter paper and 50 ml. shaken with an excess of *N*/10 sodium hydroxide solution.

[1] *Z. anal. Chem.*, 1924, **65**, 289 ; 1926, **68**, 257.

The sodium picrate solution is separated and the toluene washed twice with 100 ml. of water. Finally the excess of alkali in the aqueous layer is determined by titration with *N*/10 hydrochloric acid, using methyl red as indicator, and the picric acid content of the original filtrate is calculated from the alkali consumed.

If the cresol contains xylenol, the nitro-compounds obtained are dissolved in hot alcohol and the solution treated with naphthalene; on cooling, a double compound of naphthalene and trinitro-*m*-cresol crystallizes out (m.p. 125°), from which the weight of the nitrocresol is obtained by dividing by 1·391. Cresol containing both phenol and xylenol is analysed by a combination of the two methods.

Russig and Fortmann [1] have described a method which is used in France. This is not so simple or rapid as Raschig's method, but gives rather higher results, probably because the nitration is more complete; it is also inapplicable for mixtures containing more than 10 per cent. of phenol or xylenols. 50 g. of the cresol is weighed into a small conical flask and mixed with 125 g. of sulphuric acid of sp. gr. 1·84. The temperature of the mixture rises spontaneously to between 60° and 70° and further warming is unnecessary. After standing for one to two hours the sulphonic acid is nitrated in a tubulated 1 litre retort placed in a sand bath; the neck of the retort is connected to a wash-bottle, and this in turn to a good draught. 400 ml. of nitric acid of sp. gr. 1·38 is placed in the retort, heated to 60°, and the flame then removed. A cylindrical dropping-funnel without a neck is fixed in the tubulure of the retort by a rubber stopper, and the small conical flask in which the sulphonation was effected is placed upside-down over the funnel in such a way that the contents are only delivered slowly and are similarly emptied from below. The sulphonic acid is allowed to drop gradually into the hot nitric acid during a period of one and a half to two hours; it is thus completely nitrated and oxidized; the oxidation is accompanied by a violent development of heat and evolution of nitrous fumes. About twenty minutes after the conclusion of the reaction, the contents of the retort are poured into a dish containing 200 ml. of water, and the retort rinsed out with a further 200 ml. After standing overnight the crystalline mass is crushed in the dish, filtered on a hardened filter paper on the pump, washed with a further 200 ml. of water, and weighed. When treated in this manner 50 g. of pure *m*-cresol yields 87·8 g. of trinitro-*m*-cresol, being 175·6 per cent., whereas by Raschig's method only 174·0 per cent. is obtained on the weight of the original cresol.

8. **Analysis of Cresol Mixtures.**—Raschig [2] separates the *o*-cresol in commercial cresol by repeated fractional distillation, and obtains

[1] *Z. angew. Chem.*, 1901, **14**, 157.
[2] *Ibid.*, 1900, **13**, 759.

a distillate containing roughly 60 per cent. of *m*-cresol and 40 per cent. of *p*-cresol, in which the *m*-compound is determined by his method.

Fox and Barker [1] have worked out a process for the estimation of *m*-cresol which is dependent on bromination in a dry solvent, such as carbon tetrachloride. In such a solution and with excess of dry bromine *m*-cresol yields a tribromo-derivative, whilst phenol, *o*-cresol and *p*-cresol yield only dibromo-derivatives. About 1 g. of the dried cresylic acid is weighed into a tared flask fitted with a small ground-in tap funnel and an outlet having a glass stopcock. Excess of a solution containing 200 g. of bromine per litre in carbon tetrachloride is slowly dropped into the flask by means of the funnel and the mixture allowed to stand for several hours at ordinary temperature. Most of the bromine is then expelled by gentle warming on the water-bath, care being taken that the temperature does not exceed 50°. The apparatus is connected to the pump and the solvent very slowly distilled off at about 30 cm. pressure, the temperature of the bath being kept below 50°; the bromo-derivatives are appreciably volatile above 70°. When the flask is dry, the tap funnel and the side tube are removed and the increase in weight due to bromination is determined. The percentage of *m*-cresol equals $\frac{(100W - 246{\cdot}3)}{0{\cdot}731}$, where W is the weight of bromo-derivatives obtained from 1 g. of the mixed cresols.

Fox and Barker also describe a modification of the bromination method proposed by Ditz and Cedivoda [2]; the original method was subjected to adverse criticism by Russig and Fortmann.[3] This method is stated by Fox and Barker to be very rapid and sufficiently accurate for general work. About 1 g. of the cresol is weighed into a 200 ml. graduated flask; 5 ml. of $2N$ sodium hydroxide solution is added and the liquid diluted to the mark with distilled water. 10 ml. of this solution is placed in a well-stoppered flask of about 300 ml. capacity and excess (100 ml.) of a mixture of equal parts of $N/20$ potassium bromide and $N/100$ potassium bromate added, followed by 10 ml. of hydrochloric acid of sp. gr. 1·08. The flask is closed, sealed by running a little water round the stopper, and shaken for exactly one minute. The stopper is then removed only far enough to admit 20 ml. of a 10 per cent. solution of potassium iodide; this must be introduced so that there is always a seal round the stopper. A loss of bromine vapour is a serious source of error in the determination. The flask is placed aside for one hour and the liberated iodine is titrated with $N/10$ thiosulphate solution. Towards the end of the titration 10 ml. of carbon tetrachloride is introduced;

[1] *J. Soc. Chem. Ind.*, 1920, **39**, 169 T.
[2] *Z. angew. Chem.*, 1899, **12**, 873, 897; 1900, **13**, 1050.
[3] *Ibid.*, 1901, **14**, 160.

the solution of the mixture of bromocresol and iodine in the carbon tetrachloride gives a sharp end-point to the titration. *m*-cresol takes up 480 g. of bromine per 108 g. of cresol; *o*- and *p*-cresols require 333 g. and 332 g. of bromine respectively per 108 g. of cresol.

If Br equals the bromine actually absorbed, the percentage of *m*-cresol equals $\frac{(100\text{Br}-308)}{1\cdot364}$. The results obtained with synthetic mixtures containing *m*-cresol up to 50 per cent. are within 2 per cent. of the actual amounts present; with larger percentages (about 80 per cent.) the results are from 3 to 4 per cent. too low. In the latter case *o*-cresol should be added to the original cresylic acid to bring the percentage of *m*-cresol down to about 50 per cent. For the determination of *o*-cresol and *p*-cresol, the percentage of phenol is also determined (p. 335), and the sp. gr. at 15·5°/15·5°. It is assumed that the sp. gr. of a mixture of the three cresols is additive to the fourth decimal place, an assumption which is practically true in all cases. The values for the sp. gr. of the constituents, for this purpose, are phenol, 1·0774; *o*-cresol, 1·0516; *m*-cresol and *p*-cresol, 1·0388.

The sp. gr. and composition of a mixture are then related according to the formula: $100\ G = [1\cdot0774P + 1\cdot0388M + 1\cdot0516O + 1\cdot0388(100 - P - M - O)]$; P, M, O, and (100−P−M−O) are the percentages of phenol, *m*-cresol, *o*-cresol and *p*-cresol, respectively, and G is the observed sp. gr. at 15·5°/15·5°.

The proportion of *o*-cresol is thus obtained from the simplified expression: $0\cdot0386P + 0\cdot0128O = 100(G - 1\cdot0388)$, where O is the proportion of *o*-cresol present. If phenol is absent the equation is simply: $0\cdot0128\ O = 100(G - 1\cdot0388)$; this equation applies to all mixtures of the three cresols, such as "tri-cresol," and commercial *m*-cresol.

The results on the following page are given by Fox and Barker.

The *o*-cresol result may be as much as 3 per cent. low when much phenol is present and within 2 per cent. of the actual quantity in the absence of phenol. The fraction of cresylic acid distilling up to 195° is found nearly always to contain 65 to 75 per cent. of *o*-cresol, and if phenol is present also, the total proportion of phenol and *o*-cresol is also of the same order.

When only approximate results are rapidly required for *o*-cresol and *p*-cresol, in mixtures containing a large proportion of *o*-cresol, the refractive index of the mixture may be observed at 50°, using an Abbe refractometer. The refractive indices used for this purpose (n_D) are respectively: 1·5309 for *o*-cresol, 1·5266 for *m*-cresol, and 1·5260 for *p*-cresol.[1] The refractive index can be determined at any two convenient temperatures and the necessary correction for 50° applied.

[1] *Cf.* Pound, *Chem. and Ind.*, 1934, 53, 71.

The percentage of *o*-cresol equals $\frac{(100n_D - 0\cdot0006M - 152\cdot6)}{0\cdot0049}$, where M equals the percentage of *m*-cresol and n_D is the observed refractive index at 50°.

Nature of mixture.	Percentage determined.				
	Phenol.	*o*-Cresol.	*m*-Cresol.	*p*-Cresol.	Xylenols.
Synthetic mixture No. 1 (composition shown in brackets)	9·7 (10·0)	54·6 (55·4)	15·1 (17·1)	20·6 (17·5)	(Distilling above 205° with a Raschig column) (sp. gr. 1·0326 at 15·5°/15·5°).
Synthetic mixture No. 2 (composition shown in brackets)* . . .	4·6 (5·1)	35·2 (33·4)	30·1 (30·8)	30·1 (30·7)	...
Commercial 80 per cent. *m*-cresol . . .	1·1	nil	72·0	24·4	...
Commercial cresylic acid, commercially described as phenol-free . .	11·0	11·3	44·3	18·5	14·9
Cresylic acid containing phenol . . .	20·0	32·1	11·7	29·4	6·8
Cresylic acid containing phenol . . .	16·6	31·2	20·2	17·3	14·7
" Tri-cresol " . . .	nil	37·8	16·7	45·5	nil
Colourless cresol free from xylenols . . .	3·4	28·0	33·5	35·1	"

* Deficiency due to water.

9. **Determination of Phenol in Commercial Cresylic Acid.**—Lowe's test for the examination of crude tar acids for its yield of crystallizable phenol (p. 200) is essentially a means of broadly specifying the quality ; it is not applicable to the accurate determination of phenol in commercial cresylic acid. According to Fox and Barker's method[1] the cresylic acid is first fractionated with an efficient column up to 210°, to obtain a distillate containing all the phenol, practically all the cresols and a little xylenol. This distillate is again fractionated up to 195°, sufficient *o*-cresol being added, if necessary, to bring over all the phenol in the fraction up to 195°. The phenol is then determined in an aliquot part of this distillate by application of the crystallizing point curve for mixtures of phenol and *o*-cresol, after sufficient pure phenol has been added to give a mixture containing at least 80 per cent. of phenol. The crystallizing point curve for such mixtures is practically identical with that for mixtures containing more than 80 per cent. phenol and the distillate up to 195° obtained from commercial cresylic acid free from phenol. The method is as follows :—

100 ml. of the cresylic acid is shaken with 200 ml. of sodium hydroxide solution of sp. gr. 1·2 and the liquid extracted three

[1] *J. Soc. Chem. Ind.*, 1917, **36**, 842 ; 1918, **37**, 265 T.

times with ether, using 20 to 30 ml. of ether each time, to remove naphthalene and neutral tar oils. Benzene may be used instead of ether; the sodium hydroxide solution must, however, be boiled sufficiently strongly before acidification to expel all the benzene. Three treatments with benzene are required in amount dependent on the impurity of the cresylic acid. The ether is washed with a little water, once or twice, and the washings added to the sodium hydroxide solution which is then warmed gently to remove ether. The cooled soda solution is acidified with sulphuric acid (1 : 1), the mixture being cooled in running water during acidification; the separated tar acids are removed; the aqueous layer is extracted with ether (or benzene), and the ethereal solution added to the tar acids. Free sulphuric acid is removed from this ethereal solution by washing with nearly saturated sodium sulphate solution; the ethereal solution is then dried over freshly ignited calcium chloride (cooled in an atmosphere of carbon dioxide), the dried liquid transferred to a flask, the calcium chloride washed with dry ether, and the liquid distilled up to about 120° to remove all the ether. If benzene is employed, distillation must be carried to 140° or even higher. 100 ml. of the purified tar acids are now distilled in a 300 ml. round-bottomed flask with a neck about 5 in. long, fitted with a four-pear Young column, or a rod and disc column. A short bulb thermometer graduated in 0·5° from 90° upwards is used, the centre of the thermometer bulb being 1 cm. below the side tube of the fractionating column. Corrections must be applied for emergent stem. Distillation is carried up to 210° at a rate of 7 ml. per minute, and the distillate so obtained (A) is again fractionated up to 195° at the same rate, the distillate collected in a tared vessel and weighed. A second fraction from 195° to 196·5° is also collected separately. If the fraction distilling up to 195° amounts to about 50 per cent. of the tar acids collected in the first fractionation (A) the phenol can be estimated at once by the standard crystallizing point method (p. 227). If, however, this fraction is much less than 50 per cent., sufficient *o*-cresol is added to the first fraction (A) to yield at least 50 per cent. of distillate up to 195°. An amount of *o*-cresol equal in volume to the fraction of the first fraction (A) distilling between 195° and 202° generally suffices. Any moisture in the weighed distillate is removed by ignited calcium chloride. The crystallizing point of the distillate so determined is referred to a curve of crystallizing points of known mixtures of phenol and a mixture of cresols corresponding to the mixture under examination; the amount of phenol is so determined. The percentage of phenol in the original sample equals $\frac{W \times (C - B) \times 100}{A \times 100 \times \text{sp. gr. of sample}}$, where W is the total weight of distillate up to 195°, A equals the aliquot portion of distillate up to

195°, B is the amount of phenol added to yield a mixture containing at least 80 per cent. of phenol, and C equals the amount of phenol determined from the crystallizing point of the mixture.

The distillate collected between 195° and 196·5° is tested for phenol by placing 0·1 to 0·2 ml. of the distillate in a stoppered 100 ml. glass cylinder, adding 10 ml. of water and then three drops of hydrochloric acid of sp. gr. 1·15. The mixture is well shaken and sufficient freshly prepared saturated bromine water is added to bring the total volume to 100 ml. The cylinder is again shaken and the precipitate allowed to settle. If 5 per cent. of phenol or more is present in the original sample a voluminous light precipitate of small needles is formed; the cresols alone produce a dark oil or heavy granular precipitate which settles quickly. According to Sharples,[1] 1 per cent. of phenol can be ascertained with certainty; below this amount the results appear doubtful.

Comprehensive data relating to the boiling point, sp. gr. and crystallizing point of different mixtures of phenol and the cresols are given variously by Weiss and Downs,[2] Fox and Barker,[3] and Dawson and Mountford.[4] The following table is compiled from the data given by Weiss and Downs, but for more detailed information the original communications should be consulted.

Per cent. phenol.	Per cent. *o*-cresol.	Solidification point, °C.	Specific gravity, 25°/25°.	Specific gravity, 45°/45°.
100	...	40·4	...	1·0636
95	5	37·2	...	1·0623
90	10	34·6	...	1·0607
85	15	32·2	...	1·0594
80	20	29·0	...	1·0583
75	25	26·0	...	1·0566
70	30	23·2	1·0650	1·0554
65	35	20·4	1·0636	...
60	40	19·2	1·0621	...
55	45	19·2	1·0605	...
50	50	19·2	1·0596	...
45	55	19·6	1·0583	...
40	60	20·0	1·0567	...
35	65	20·6	1·0555	...
30	70	21·7	1·0541	...
25	75	22·6	1·0524	...
20	80	23·8	1·0509	...
15	85	24·4	1·0493	...
10	90	25·8	1·0479	...
5	95	27·0	1·0464	...
...	100	29·0	1·0444	...

The phenol was a close-cut middle fraction from the final distillation of synthetic phenol; the *o*-cresol was a purified *o*-cresol fraction, separated and fractionated to give a cresol boiling within about 2°.

[1] *J. Soc. Chem. Ind.*, 1918, **37**, 109 T. [2] *Ind. Eng. Chem.*, 1917, **9**, 569.
[3] *J. Soc. Chem. Ind.*, 1917, **36**, 842; 1918, **37**, 268 T.; 1920, **39**, 169 T.
[4] *J. Chem. Soc.*, 1918, **113**, 923.

Knight, Lincoln, Formanek and Follett[1] describe a somewhat lengthy method for the determination of phenol in cresylic acid whereby reference to graphs is obviated. The method is based upon the sp. gr. and crystallizing point of a mixture of the purified and fractionated tar acids and *o*-cresol, and the same values for a mixture of the purified and fractionated tar acids and phenol.

Hoffert[2] states that the methods employed by Fox and Barker and Dawson and Mountford are difficult of application; even using an efficient column it is only when the phenol content is very low that all the phenol passes over in the distillate up to 191°, which is given as the boiling point of *o*-cresol (*cf.* p. 455). Hoffert bases his method on the determination of the crystallizing point of phenol hydrate in mixtures of phenol and the cresols containing at least 55 per cent. of phenol and 10 per cent. of its weight of water. The lowering of the crystallizing point of phenol hydrate by each of the three cresols is the same within the limits of experimental error. The method is as follows:—

If the sample of cresylic acid contains more than 2 to 3 per cent. of impurities in the form of neutral hydrocarbons and pyridine bases, these are removed either by steam distillation of the sodium hydroxide solution or by extraction with ether or benzene as described previously (p. 198). In recovering the tar acids by acidification of the alkaline solution with sulphuric acid any phenol present in the sodium sulphate solution must be recovered. If the tar acids distil over entirely below 205°, the determination of the phenol may be at once begun. If, however, more than a trace of xylenols and higher homologues is indicated, they must be removed by a preliminary fractionation to 203°, using an efficient column. The mixture of tar acids so obtained must be freed from water. A known weight of pure phenol is then added to a weighed portion of the dried tar acids mixture to yield a mixture containing at least 55 per cent. of phenol, and 10 per cent. of its weight of water is run in from a burette. 12 to 15 g. of the resulting solution is used for the determination of the crystallizing point. During the determination, the solution should be seeded with a crystal of phenol hydrate to ensure that phenol hydrate crystallizes out and not mixed crystals of phenol and the cresols. The crystallizing point is taken as the temperature at which the phenol hydrate crystals just disappear when the apparatus is removed from the cooling bath and placed in a water-bath cooled with ice to a temperature 1° to 2° above the crystallizing point of the mixture as ascertained in a preliminary determination. Successive determinations should not differ by more than 0·1°.

[1] *Ind. Eng. Chem.*, 1918, **10**, 9.
[2] *J. Soc. Chem. Ind.*, 1922, **41**, 334 T.

The percentage of phenol is read off from a curve constructed from the following data :—

Per cent. phenol in mixture.	Crystallizing point of hydrate (0·1 per cent. water.)
100	16·0
95	14·25
90	12·25
85	10·25
80	8·1
75	5·8
70	3·4
65	0·75
60	—2·2
55	—5·2

If the percentage of phenol so ascertained is p, a is the weight of original mixture taken, and b the weight of pure phenol added, then the percentage of phenol in the mixture is $\frac{(p(a+b)-100b)}{a}$.

The method is rapid and generally applicable as a work's test, and the effect of small traces of moisture in the phenol-cresol mixture is practically negligible. The method may be used for the determination of phenol in crude carbolic acid.

Masse and Leroux [1] fractionally distil a large quantity of cresylic acid and estimate the phenol in the fractionated tar acids (after enrichment with phenol), by a determination of the crystallizing point of the final distillates.

The Standard Method for the determination of phenol in phenol-cresol mixtures, containing 20 per cent. or more of phenol, is accurate for ordinary commercial mixtures in which the phenol appears with orthocresol and smaller amounts of the other cresols. If special precautions are taken, errors up to 1 per cent., which would otherwise arise, can be eliminated.[2]

The test is carried out on the dried sample; if the water content does not exceed 1 per cent., 100 ml. is distilled from a standard distillation flask using the side arm as a condenser and distilling off 2 ml. The flask is then allowed to cool with a calcium chloride tube attached to the side arm; the contents of the flask are used for test. If the water exceeds 1 per cent., 250 ml. is distilled from a round-bottomed flask through a standard 12-bulb pear column and a standard air condenser. The phenols in the distillate to 170° C. are salted out by the addition of powdered sodium chloride and the undistilled sample having cooled, the separated phenols are added back; 100 ml. of the well-mixed material is treated for the removal of final traces of water as in the case of samples originally containing less than 1 per cent. of water.

[1] *Compt. rend.*, 1916, **163**, 361. [2] *J. Chem. Soc.*, 1918, **113**, 923.

The crystallizing point of the dried sample is determined by the Standard Method; if it is 27·0° C. or higher, the fractional phenol content is obtained from the table on p. 203; the percentage in the original sample is calculated as P $(100-w)$ where P is the fractional phenol content read from the table on p. 203 and w is the percentage water content obtained by the method described on p. 344.

If the crystallizing point is below 27·0° C. about 20 g. of the dried sample is weighed into a standard distillation flask and about four times the weight of 99/100 phenol is added. The contents of the flask are dried by side arm distillation of 2 ml. as before. The fractional phenol content of the mixture is ascertained by determination of the crystallizing point and reference to the table on p. 203. The percentage by weight of phenol in the original sample is

$$\frac{(PW_1+PW_2-P_1W_2)\,(100-w)}{W_1}$$

where

w = the percentage by weight of water in the sample, determined by the method described on p. 344.

W_1 = the weight of the dried sample used for the crystallizing point determination;

W_2 = the weight of the phenol added;

P = the fractional content of pure phenol in the mixture used for the crystallizing point determination; and

P_1 = the fractional content of pure phenol in the phenol added.

The percentage of phenol read from the table on p. 203 is accurate for ordinary commercial coal tar phenol-cresol mixtures, in which the phenol is present with orthocresol and smaller amounts of meta- and paracresol. If special mixtures, such as phenol with meta- and para-cresol, are under examination, errors up to ± 1 per cent. on the phenol content may arise. In such cases, a special table of crystallizing points should be prepared, using the same diluent for phenol as is present in the sample under examination.[1]

Standard Methods adopts Chapin's use [2] of Millon's reagent for the determination of phenol in cresylic acids containing less than 20 per cent. of phenol; it is also available when the composition of the sample rules out other methods. This highly sensitive reagent is especially useful when only limited amounts of sample are available. The underlying principle is the bleaching effect of formaldehyde on the colour developed by treating phenol with Millon's reagent, the colour developed with the higher phenols remaining unchanged.

Dilute nitric acid is prepared for the test by bubbling air through concentrated acid until the acid is colourless, and then diluting

[1] Dawson and Mountford, *J. Chem. Soc.*, 1918, **113**, 923.

[2] *United States Department of Agriculture Bulletin*, No. 1308, 22nd November 1924.

1 volume of acid with four of water. Millon's reagent is prepared under controlled conditions, as described earlier (see p. 321); it must be used within thirty-six hours of preparation.

A stock phenol solution is made of 1 per cent. strength; from this a standard test dilution is prepared, containing exactly 0·025 per cent. of phenol. The formaldehyde solution is the usual 40 per cent. material of commerce diluted to the extent of 2 ml. in 100 ml. of aqueous solution.

2·5 g. of sample is dissolved in 10 ml. of 10 per cent. caustic soda solution and made up to 250 ml.; 5 ml. of this solution is taken in a 200 ml. graduated flask, diluted with water and the dilute nitric acid added until neutrality to methyl orange (one drop) is reached; the solution is made up to the mark.

5 ml. of the resulting solution is pipetted into each of two test-tubes, A and B. Into each of two further tubes, C and D, 5 ml. of the standard phenol solution is pipetted; 5 ml. of the Millon's reagent is measured from a burette into each of the four tubes and all the tubes placed in a water-bath at 100° C. for exactly thirty minutes. The tubes are then immediately and thoroughly cooled in a bath of cold water for at least ten minutes; 5 ml. of the dilute nitric acid reagent is added to each tube and the tubes shaken gently to effect mixture of the contents. 3 ml. of the formaldehyde solution is added to tubes A and C; the contents of each tube are diluted to 25 ml. with water, the tubes stoppered and allowed to stand overnight after shaking.

20 ml. of the contents of tubes C and D are pipetted into separate 100 ml. graduated flasks, C and D respectively; 5 ml. of the dilute nitric acid reagent is added to each flask and the contents made up to 100 ml.; two burettes, C and D, are filled from the respective flasks, burette C containing yellow "phenol blank" and D containing orange "phenol standard" solution.

10 ml. of the contents of tubes A and B, "sample blank" and "sample unknown" respectively, are measured into separate Nessler cylinders (matched), A and B respectively; expeditiously, equal volumes of phenol standard and phenol blank are run from the burettes into sample blank and sample unknown respectively, in small increments, until with intermediate stoppering and thorough shaking of the cylinders, the contents of the cylinders are matched in colour.

If exactly 2·5 g. of sample was used originally, each ml. of phenol standard used in the colour-matching process corresponds to 2 per cent. by weight of phenol in the sample. The amount of phenol standard used must not exceed 10 ml.; if it does, the test must be regarded as a trial and repeated from the stage of measuring into the Nessler cylinders, taking a smaller quantity than 10 ml. of the

contents of tubes A and B and making up to 10 ml. with a 1 : 4 mixture of the dilute nitric acid reagent and water.

10. **Determination of Orthocresol in Commerical Cresylic Acid.**—Potter and Williams [1] employ the reverse of Cocking's well-known method for the determination of cineole in eucalyptus oils.[2]

Relation between Crystallizing Point and Orthocresol Content of Orthocresol-Cineole Mixtures

Crystallizing point °C.	0·0.	0·1.	0·2.	0·3.	0·4.	0·5.	0·6.	0·7.	0·8.	0·9.
	Percentage of Orthocresol by Weight.									
31	40·0	40·2	40·3	40·5	40·6	40·8	40·9	41·1	41·2	41·4
32	41·6	41·7	41·9	42·0	42·2	42·4	42·5	42·7	42·9	43·0
33	43·2	43·4	43·5	43·7	43·9	44·0	44·2	44·4	44·5	44·7
34	44·9	45·0	45·2	45·4	45·6	45 8	46·0	46·2	46·3	46·5
35	46·7	46·9	47·1	47·3	47·5	47·7	47·9	48·0	48·2	48·4
36	48·6	48·8	49·0	49·2	49·4	49·6	49·8	50·0	50·2	50·4
37	50·6	50·8	51·0	51·2	51·4	51·6	51·8	52·0	52·2	52·4
38	52·6	52·8	53·0	53·2	53·4	53·6	53·8	54·0	54·2	54·5
39	54·7	54·9	55·1	55·3	55·5	55·7	56·0	56·2	56·4	56·6
40	56·8	57·0	57·2	57·4	57·6	57·8	58·0	58·2	58·4	58·6
41	58·8	59·0	59·3	59·5	59·7	60·0	60·2	60·4	60·6	60·8
42	61·0	61·3	61·5	61·7	62·0	62·2	62·4	62·6	62·9	63·1
43	63·3	63·6	63·8	64·0	64·3	64·5	64·8	65·0	65·2	65·5
44	65·8	66·0	66·2	66·4	66·7	66·9	67·2	67·4	67·6	67·8
45	68·0	68·3	68·5	68·8	69·0	69·3	69·5	69·8	70·0	70·3
46	70·5	70·8	71·0	71·3	71·6	71·8	72·1	72·4	72·6	72·9
47	73·1	73·4	73·7	73·9	74·2	74·5	74·7	75·0	75·2	75·5
48	75·7	76·0	76·3	76·5	76·8	77·0	77·3	77·6	77·8	78·1
49	78·3	78·6	78·9	79·2	79·4	79·7	80·0	80·2	80·5	80·8
50	81·1	81·4	81·7	82·0	82·3	82·6	82·8	83·2	83·4	83·7
51	84·0	84·3	84·6	84·9	85·2	85·5	85·8	86·1	86·4	86·7
52	87·0	87·3	87·6	87·9	88·2	88·5	88·8	89·1	89·4	89·7
53	90·0	90·3	90·6	90·9	91·2	91·5	91·8	92·1	92·4	92·7
54	92·9	93·2	93·5	93·8	94·1	94·4	94·7	95·0	95·3	95·6
55	95·9	96·2	96·5	96·8	97·1	97·4	97·7	98·0	98·2	98·5
56	98·8	99·1	99·4	99·7	100·0	...	...	...	...	...

The Standard Method for the determination of orthocresol in cresylic acid is that of Potter and Williams, developed [3] by subsequent investigations in conjunction with the authors. As described in outline above it is applicable only to material containing 40 per cent. or more of orthocresol, but samples deficient in orthocresol may be tested by the method after adding an appropriate known amount of pure orthocresol.

[1] *J. Soc. Chem. Ind.*, 1932, **51**, 59. [2] *Pharm. J.*, 1920, **105**, 81.

[3] "Standardization of Tar Products Tests Committee," *J. Soc. Chem. Ind.*, 1938, **57**, 212.

The sample is first dried by the method or methods described on p. 339 in connection with the determination of phenol in phenol-cresol mixtures. 8·40 g. of the dried sample and 12·00 g. of pure cineole are weighed into the inner tube of the standard crystallizing point apparatus (Fig. 35) and the apparatus assembled with a standard thermometer having a range of 15° to 45° C. (for mixtures testing below 42° C.) or 39·5° to 70·5° C. (for mixtures testing 42° C. or over).

The crystallizing point of the mixture is determined and the percentage of orthocresol is found by reference to the preceding table (provided the crystallizing point of the cineole used lies between 1·2°

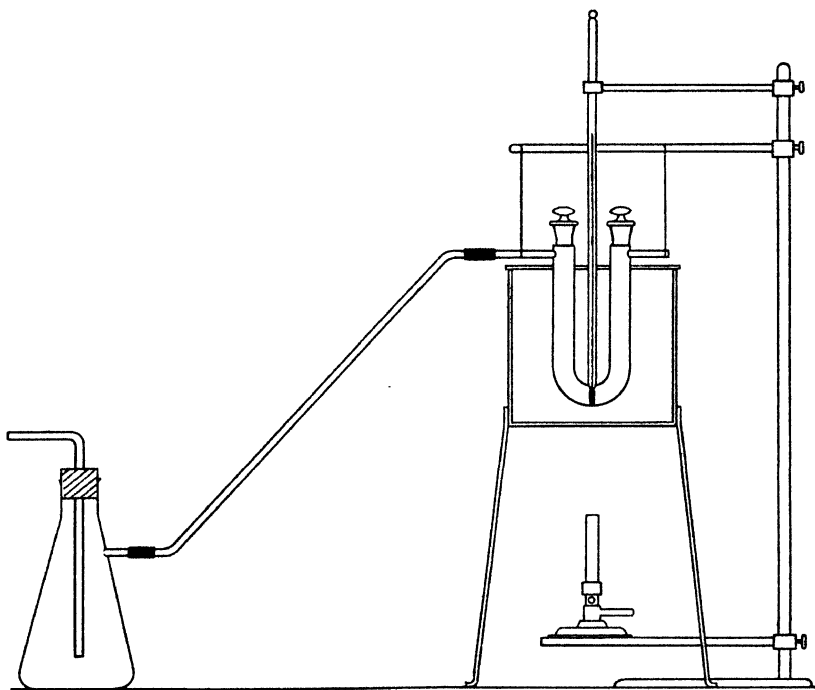



Fig. 48.—Residue on Evaporation of Phenols and Refined Cresylic Acids—Assembled Apparatus.

and 1·4° C.) or to a special table prepared by the analyst, using the same cineole as used in the test and various mixtures of known orthocresol content. The table is based on crystallizing points of mixtures made from dried samples and, if water was present in the original sample, an allowance must be made. The test is said to be accurate to within one half of one per cent.

11. **Residue on Evaporation.**—The residue on evaporation of several refined commercial products in this series, notably of phenol and the separate cresol isomers, is of commercial significance and a Standard Method is available.

The apparatus is shown in Fig. 48. The stoppers of the U-tube must not be greased; for convenience the air-bath is constructed in copper; the thermometer must have an upper limit of at least 155° C.

The empty U-tube is thoroughly dried by heating it in the bath to 150° C. ±5°, while a gentle stream of clean air is drawn through it. It is allowed to cool with a calcium chloride tube fitted to one side arm and the other side arm closed; it is then weighed. About 10 g. of sample is introduced into the bottom of the tube, the tube and contents weighed, the apparatus reassembled as shown and the heating repeated under the same conditions as before until evaporation is complete. Cooling and weighing follow and then further heating, cooling and weighing until the weight remains constant.

12. **Hydrogen Sulphide.**—Hydrogen sulphide is an objectionable constituent and the British Standard Specifications require substantial freedom from it. No permissible numerical limit is given, so the Standard Method is on qualitative lines: 20 ml. of the sample is placed in a 100 ml. conical flask, the mouth of which is covered with a piece of filter paper moistened with 10 per cent. lead acetate solution. After five minutes on a boiling water-bath, the paper is examined; a coloration deeper than pale yellow indicates the presence of hydrogen sulphide.

13. **Water.**—The water in refined products is determined by the Dean and Stark method; it is only necessary to note that, using 100 ml. of sample, 100 ml. of solvent naphtha is added to the boiling flask to facilitate distillation of the water.

(*e*) Solutions containing Soap and Phenol or Cresol

These comprise sapocarbol, lysol, creolin, carbolic soap and similar preparations. They cannot be examined by any of the methods described previously as the fatty acids interfere, and they must therefore be systematically separated into hydrocarbons, phenols and fatty acids if a full analysis be required.

Ditz and Clauser [1] analyse lysol by the following method, which is applicable also to all mixtures of phenols with fatty acids and their salts (soaps). 5 g. of lysol is dissolved in 100 ml. of luke-warm water, and 20 to 30 ml. of 10 per cent. sodium hydroxide solution added, so that the phenols are completely converted into their alkali salts. The hydrocarbons are then extracted by shaking two to three times with ether, which is afterwards freed from traces of dissolved phenates by shaking with dilute sodium hydroxide solution which is then added to the main alkaline solution. The ethereal extracts are dried with anhydrous potassium carbonate, which is afterwards washed with a little dry ether, carefully evaporated, and the residue dried over

[1] *Chem.-Ztg.*, 1898, **22**, 732.

strong sulphuric acid until the weight is constant. The alkaline solution containing the phenols, etc., is freed from ether by warming on the water-bath and neutralized with hydrochloric acid. The point of neutrality is easily recognized by the first signs of turbidity. The solution is then cooled and treated with an excess of barium chloride and with titrated barium hydroxide solution, about equivalent in quantity to the cresol which is present. The barium oleate must be precipitated in the cold, or it separates in an unsatisfactory condition. After stirring for a short time, the liquid is filtered as rapidly as possible, in order to avoid decomposition of the cresolate and the production of turbidity in the filtrate by the carbon dioxide in the air. The precipitated barium oleate is first washed with water containing a little barium hydroxide and finally with hot distilled water. It is then rinsed into the beaker in which the precipitation was effected, decomposed with hydrochloric acid, filtered through the same filter as before, and the fatty acid examined and estimated by any of the ordinary methods. The cresols, freed from fatty acids, are now present in the filtrate, and can be determined gravimetrically by acidifying and extracting with ether. It is more accurate to dilute the acidified filtrate to a definite volume and determine the cresols volumetrically by Koppeschaar's method (p. 328), the mean of several estimations being taken. In this way the mean bromine value of the total phenols is obtained. As the relative proportion of the various phenols of which the mixture consists is unknown, a supplementary determination is made of the bromine-absorbing power of a weighed quantity of the mixed phenols. For this purpose a convenient quantity of the acidified filtrate is shaken out with ether, the solvent evaporated, and after drying at 100° to 110°, the residue weighed and titrated with bromine by Koppeschaar's method. Any loss of the phenols during their isolation for this purpose is obviously of no consequence, since their relative proportion will not be affected. The percentage of phenols is then given by the formula $\frac{100 \times a \times d}{b \times c}$, where a is the weight of bromine equal to the total phenols, d the weight of the phenols from the ethereal extract, b the weight of bromine absorbed by the same, and c the weight of lysol used for the analysis.

For the purposes of this investigation, Koppeschaar's method must be modified by dissolving 9 parts of the bromide-bromate mixture in 1000 instead of 100 parts of water ; moreover, after liberating the bromine with sulphuric acid, the liquid must be allowed to stand for half an hour so that the reaction may be quite complete ; also, on titrating back with thiosulphate solution, the liquid should again be allowed to stand for a quarter of an hour after decolorization, so that the blue colour which usually reappears may be completely removed

by further addition of thiosulphate. According to Dodd,[1] separation of the calcium or barium salts of the soap only succeeds with certain fatty acids such as oleic acid.

The following tests for liquor cresolis saponatus are specified in the *British Pharmacopœia* [2] :—

1. When 5 ml. is mixed with 95 ml. of water a clear solution must be formed which shows no opalescence on standing for not less than three hours.

2. When 5 ml. is diluted with 50 ml. of neutralized 95 per cent. alcohol and titrated with normal sulphuric acid, using a solution of alkali blue as indicator, not more than 0·3 ml. must be required (limit of alkali). Alkali blue is a mixture of the sodium sulphonates of phenylated rosaniline and *para*-rosaniline ; the solution contains 0·1 per cent. by weight of alkali blue in 90 per cent. alcohol.

3. The liquid must pass the lead acetate test for sulphuretted hydrogen.[3]

4. Distil 120 ml. until all the water and 50 ml. of cresol have been collected. The cresol thus recovered must comply with the test for the limit of hydrocarbons and the limit for volatile bases specified for Cresol B.P. In making these tests the aqueous portion of the distillate is used instead of an equal volume of water.

5. 250 ml. is weighed accurately into a separating funnel, 100 ml. of ether added together with a slight excess of hydrochloric acid, the mixture shaken vigorously and allowed to separate. The ethereal liquid is transferred to a round-bottomed flask, the aqueous liquid washed with a little ether, and the ether washings added to the contents of the flask. The ether is removed and the residual liquid steam distilled, the flask being heated in an oil bath at 170°. After the condensate has ceased to show any opalescence the distillation is continued until a further 250 ml. has been collected and the liquid condensed shows not more than a faint haze with a solution of bromine. The distillate is transferred to a separator, saturated with sodium chloride, and then extracted with three successive quantities of 100 ml. of ether. The ether is removed from the mixed ethereal solution by distillation in a tared flask, and the residual liquid heated in an oil bath at 170° to remove ether and moisture, and the crude cresol then cooled and weighed. The crude cresol is now distilled through a Liebig's condenser, any aqueous distillate being separated and measured. The non-volatile portion is transferred to a small tared dish, using a little ether. The dish is heated rapidly until fumes are given off, allowed to cool and weighed. The weights of the non-volatile residue and of the water so obtained are subtracted from the weight of the crude cresol. The separated cresol must comply with the requirements for sp. gr. and boiling range for Cresol B.P.[4] The specific gravities of the cresol with soap under assays and of the cresol solution separated from it are determined and the percentage by volume calculated.

Separation of the phenols by means of steam distillation is the official method of the *German Pharmacopœia* (Vol. 5), and is also employed by the United States Department of Agriculture [5] for the analysis of "Liquor cresolis compositus." The one serious objection to this method is the presence of higher-boiling phenols in the commercial cresylic acids used in the manufacture of different brands of lysol, which are difficult to volatilize in steam, especially in the presence of

[1] *J. Soc. Chem. Ind.*, 1924, **43**, 93 T.
[2] *British Pharmacopœia*, London, 1932 edn., p. 258. [3] *Ibid.*, p. 344. [4] *Ibid.*, p. 137.
[5] *The Analysis of Coal Tar Creosote and Cresylic Sheep Dips*, Chapin, 1908.

fatty acids. A large volume of distillate is obtained, even if the whole of the tar acids can be volatilized, from which latter the tar acids have to be extracted by means of ether. Alternatively the phenates in the steam distillate may be formed, concentrated, and the phenols liberated by acidification and measured, or the change in volume of sodium hydroxide solution may be noted when the phenols are dissolved in it. Schmatolla [1] favours the former alternative and Spalteholz [2] the latter, the tar acids being extracted from the steam distillate with benzole and added to a 1 : 3 sodium hydroxide solution. Dodd [3] considers the simple method of Jordan and Southernden [4] unsatisfactory and describes in detail a distillation method for the separation of the tar acids from the fatty acids, etc. McCarley [5] describes a convenient and satisfactory method for the analysis of disinfecting fluids of low phenol content (up to 5 per cent.), which is more rapidly carried out than the distillation-soda method and gives comparable results.

Dayk [6] has proposed the following simple method for the estimation of soap in tar emulsions. About 20 g. of the sample is placed in a beaker and treated with a known volume of warm water, and a solution of cane-sugar added until a clear syrup results. The whole is warmed on the water-bath until the liquid separates into two layers, then transferred to a separating funnel whilst still warm, and the lower aqueous solution run into a concentrated brine solution. Any soap present separates out completely and is filtered off, washed with brine solution, allowed to dry, and purified by recovery from alcohol solution.

(*f*) Disinfectant Powders

These usually consist of mixtures of various inorganic materials with varying quantities of cresol, crude carbolic acid, or tar oils. Slaked lime, powdered gypsum, or levigated chalk are the ordinary mineral constituents. Less common preparations are prepared by using as carriers certain anhydrous compounds such as boric anhydride, aluminium oxide, magnesium oxide, or dehydrated salts, such as calcined borax, alum, or salts of pyro- and meta-phosphoric acids. These salts form solid addition compounds with phenols, in which the latter take the place of water of crystallization. Other preparations are made by impregnating porous materials such as cardboard and gypsum plates or porous earthenware with carbolic acid.

The active constituents of the above-mentioned and other similar preparations, which consist of phenols and tar oils, are separated by distillation in a current of steam or by extraction with ether, after first acidifying, should basic constituents be present. They are then

[1] *Chem.-Ztg.*, 1922, **46**, 661. [2] *Ibid.*, 1898, **22**, 58. [3] *Loc. cit.*
[4] *Pharm. J.*, 1921, **106**, 479. [5] *J. Soc. Chem. Ind.*, 1932, **51**, 38 T.
[6] *Corps Gras. Ind.*, 1908, No. 10.

further examined by any of the methods described above. Staveley[1] has criticized a number of proposals in this connection, including those of Williams[2] and of Muter and de Koningh.[3]

Swoboda[4] uses the following method, which gives sufficiently accurate results :—

20 g. of the sample is shaken in a litre flask with 50 ml. of 20 per cent. potassium hydroxide solution, the mixture allowed to stand for fifteen minutes, the contents made up to 1 litre and well mixed. After standing for some time the liquid becomes clear and the non-phenols rise to the surface. 50 ml. of the clear liquid is drawn off, of which the first 25 ml. is used for a determination of the phenols by Koppeschaar's method. The percentage of active phenols in the 20 g. of the sample originally taken is found by multiplying by 39·16 the amount of bromine absorbed by the 25 ml. of solution.

A British Standard specification for Disinfectant Powders is in course of preparation.[5] It is proposed that the specification shall apply to carbolic and other powders, and that the clauses relating to carbolic powders shall be as follows :—

1. *Fineness.* 100 g. of the powder sieved through a British Standard 10-mesh Test Sieve[6] shall not give more than 1 per cent. oversize.
2. *Germicidal Efficiency.* A solution of the soluble part of the powder is prepared under aseptic conditions by adding a weighed portion of the powder to the requisite volume of sterile distilled water, shaking frequently in a sterile stoppered cylinder for half an hour, and filtering under aseptic conditions. The solution is tested by the Rideal Walker technique,[7] when the Rideal Walker coefficient must not be less than 0·5.
3. *Phenols.* If a phenols content less than 15 per cent. is specified, the Rideal Walker coefficient may be less than 0·5. The phenol determination is applicable only to powders containing phenols absorbed on a neutral base, *e.g.* chalk or kieselguhr, with which the phenols do not combine chemically. 50 g. of the powder is mixed intimately in a mortar with 20 g. of powdered magnesium carbonate. The mixture is then heated (gently at first) in a 250 ml. resistance glass retort. When the bulk of the oils has distilled, the retort is gently agitated, and heating continued until distillation of the oils ceases. Any condensed oils in the retort tube are forced (by heating) into the 25 ml. graduated cylinder used for collection. The volumes of oils (V_1) and of the aqueous liquor (V_2) are read and the corrected volume of oils taken as $V_1+\frac{V_2}{10}$. The contents of the cylinder are poured into a 50 ml. separating funnel and the cylinder washings (three successive portions of caustic soda solution of density 1·145 at 20°, each equal in volume to the volume of the oil) added to the separating funnel. The funnel and contents are warmed on the water-bath for ten minutes, shaken and allowed to stand to effect separation. The neutral oils are run into a 10 ml. graduated

[1] *Chem.-Ztg.*, 1889, **13**, 1126.
[2] *J. Soc. Chem. Ind.*, 1888, **7**, 826.
[3] *Analyst*, 1887, **12**, 191.
[4] *Chem.-Ztg.*, 1891, **15**, 1041.
[5] Dated 17th April 1939. Quoted by permission of the *British Standards Institution.*
[6] *B.S.* 410, 1931
[7] *B.S.*, 541, 1934. (Under revision.)

cylinder[1] and measured. Centrifuging may be necessary to effect separation. If the volume of the neutral oils is V_3, then the per cent. phenols

$$= 2(V_1 + \frac{V_2}{10} - V_3).$$

4. *Lime Base Powders.* These can only be evaluated by their germicidal efficiency (see clause 2) as no satisfactory phenols content determination is available.

VII. PYRIDINE BASES

(a) Properties

The bases in coal tar belong mainly to the pyridine and quinoline series ; small quantities of pyrrole and of aromatic bases, such as aniline, are also present. Pure pyridine, pyridine bases or commercial pyridine of different qualities, heavy or high-boiling bases, quinoline and isoquinoline are commonly marketed ; acridine is also sold as a laboratory preparation.

Pure pyridine is used as a solvent and for synthetic purposes. It is a colourless liquid of sp. gr. 0·978, and boils at 115·3° ; it gives a perfectly clear solution when mixed with water. Commercial pyridine is also used as a solvent, for the manufacture of homologues of pyridine, for the denaturing of spirit and in the textile industries, as

Base.	Melting point of base.	Boiling point at 760 mm.	Melting point of sulphate.
Quinoline	−15°	238·05°	164·0° to 164·5°
2-Methyl quinoline	−2° to −1°	247·60°	214·5° „ 215·0°
3-Methyl quinoline	+16° „ +17°	259·55°	174·5° „ 175·0°
4-Methyl quinoline	+9° „ +10°	264·20°	227·0° „ 227·5°
5-Methyl quinoline	+19°	262·70°	148·0° „ 148·5°
6-Methyl quinoline	about −22°	258·60°	176·0° „ 176·5°
7-Methyl quinoline	+39·0°	257·60°	178·0° „ 178·5°
8-Methyl quinoline	not solidified	247·75°	185·9° „ 186·1°
Isoquinoline	+24·8°	243·25°	209·0° „ 209·5°
1-Methyl-isoquinoline	+10·1° to 10·4°	255·25°	255·5° „ 256·0°
3-Methyl-isoquinoline	+64·7°	252·25°	154·5° „ 155·0°
2·8-Dimethyl-quinoline	+23·3° „ 23·6°	255·25°	194·7° „ 195·0°
1·3-Dimethyl-isoquinoline	+29·8° „ 30·0°	262·40°	242·0° „ 243·0°

a levelling agent under the name of Tetrakarnit. Commercial pyridine is usually considered to be the fraction boiling between 90° and 140° to 160°, and should be miscible in all proportions with water to give a clear solution. Heavy or high-boiling bases are not completely miscible with water and boil between about 160° and 250°. They form

[1] *British Standards Institution, B.S.* 604, 1935.

a liquid with a penetrating and unpleasant odour, generally of a dark-brown colour and impure owing to the presence of neutral compounds. They find a use as solvents, and in the isolation of carbazole and anthracene from crude anthracene.

Jantzen [1] gives the properties of homologues of quinoline, obtained from coal tar by close fractionation and by utilizing their different basicities (table, p. 349).

According to Wirth,[2] acridine (m.p. 107° ; b.p. 346°) is converted to the colourless salt, sodium 9.10.dihydroacridine-9-sulphonate by a boiling aqueous solution of sodium bisulphite ; the acridine may be recovered by treatment of this salt with alkali-hydroxide solution. By this means acridine can be separated from anthracene oil.

(*b*) The Examination of Pyridine Bases

The sale and purchase of refined pyridine are almost completely controlled by the German specification for pyridine as a denaturant or by the slightly varied versions of the German specification adopted in other countries. There are deficiencies in the specification requirements in regard to testing technique, but so long as that is a feature of the specifications, the presentation of improved methods of test finds no encouragement ; (the method for the determination of water is especially open to grave criticism). *Standard Methods*, therefore, merely describes, as precisely as possible, the general interpretation of the somewhat cursory treatment of the testing technique given in the specifications. Brief particulars are given below :—

1. **Specific Gravity.**—This may be determined by any of the usual recognized Standard Methods ; the sp. gr. bottle is obviously indicated.

2. **Colour.**—0·1 *N* iodine solution diluted with water is the basis of the specification requirements in regard to colour, and the Standard Method involves the comparison of 50 ml. of the sample and of the specified iodine solution in matched Nessler cylinders. It is recommended that the comparison be made while the cylinders are held vertically above an opaque opal glass sheet reflecting diffused daylight.

3. **Water.**—20 ml. of the sample is shaken with 20 ml. of 37 per cent. caustic soda solution in a cylinder graduated in tenths of a ml. The cylinder and contents are allowed to stand for six hours and the decrease in volume of the pyridine layer is reported as the water content of the 20 ml. of sample used.

[1] *Das fraktionierte Destillieren und das fraktionierte Verteilen als Methoden zur Trennung von Stoffgemischen, Berlin,* 1932.

[2] G.P. 440771, 1928 ; Lehmstedt and Wirth, *Ber.*, 1928, **61**, 2044 ; Lehmstedt, *Chem.-Ztg.*, 1929, **53**, 237.

4. **Distillation.**—The specifications contain no details of the apparatus apart from the special distillation flask illustrated in Fig. 49. *Standard Methods* has therefore recommended only reasonable ancillary units, including a standard thermometer (50° to 210° C. in 0·5°) fitted with its bulb in the middle of the expansion in the neck of the flask; a standard draught screen carrying an asbestos board with a 30 mm. central hole in which the flask fits snugly; a standard Liebig condenser with bent end, and a standard 100 ml. Crow receiver. 100 ml. of the sample is distilled at the uniform rate of 5 ml. per minute, the measurements of temperature and volumes of distillate being determined by the specification which is being followed.

Fig. 49.—Distillation of Refined Pyridine Bases—Distillation Flask.

5. **Congo Red Test.**—10 ml. of a 10 per cent. aqueous solution of the sample is titrated against *N* sulphuric acid, spotting on to freshly prepared Congo red test paper, until a drop of the mixture produces a distinct blue border which soon disappears.

6. **Cadmium Chloride Test.**—10 ml. of a 1 per cent. aqueous solution of the sample is shaken with 5 ml. of 5 per cent. cadmium chloride solution and the mixture allowed to stand for ten minutes. If desired the weight of the precipitate which results may be determined by filtration and drying of the material on the filter paper for one hour at 50° to 70° C., followed by weighing.

7. **Nessler's Reagent Test.**—5 ml. of Nessler's reagent is added to 10 ml. of a 1 per cent. solution of the sample; the colour of the resulting precipitate is noted.

8. **Miscibility with Water.**—20 ml. of the sample is shaken with 40 ml. of distilled water and the opalescence or otherwise of the solution is noted.

9. **Pyridine Bases for Denaturing Alcohol.**—The Reichsmonopolverwaltung für Branntwein requires that the mixture of pyridine bases used in Germany for denaturing alcohol must conform to the following :—

The colour must not be darker than that of 2 ml. of *N*/10 iodine solution in 1 litre of distilled water; with cadmium chloride solution

a distinct crystalline precipitate must be formed within ten minutes, and the filtered and dried precipitate from 10 ml. of pyridine bases must weigh not less than 25 mg.; with Nessler's solution a white precipitate must be obtained; on distillation of 100 volumes of the pyridine bases at the normal atmospheric pressure of 760 mm. at least 50 volumes should distil over up to a temperature of 140°, and 90 volumes up to 160°; a perfectly clear or only faintly opalescent solution should be obtained under the conditions of the miscibility with water test; a maximum water content of 7·5 per cent. is permitted and the Congo-red alkalinity reaction should not appear with less than 9·5 ml. of normal sulphuric acid. A further test is applied, namely, the sodium peroxide test. In this test 80 ml. of denatured alcohol is mixed with 20 ml. of pyridine bases in a 100 ml. glass-stoppered measuring cylinder, 5 ml. of freshly prepared sodium peroxide solution added, and the whole thoroughly shaken. To prepare the sodium peroxide solution, 5 g. of sodium peroxide is carefully and slowly added to 50 ml. of water contained in a flask which is continuously cooled in ice-water. The flask and contents are then warmed in a stream of water until the sodium peroxide hydrate goes into complete solution. The pyridine base mixture is allowed to stand for two hours, and its colour then compared with that of a freshly prepared iodine solution containing 2 ml. of *N*/10 iodine solution in 1 litre of distilled water. The colour of the pyridine base mixture should not be darker than the colour of the iodine solution.

(*c*) The Examination of Refined Heavy Bases

The Standard Methods for the examination of refined heavy bases comprise the determination of the sp. gr. (or density) and a distillation test, both of which are the same as the corresponding tests for refined pyridine bases; and a test for solubility in acid. The last is carried out by measuring into a standard phenols flask 50 ml. of the sample, 120 ml. of 30 per cent. hydrochloric acid and 30 ml. of water. The contents of the flask are thoroughly mixed and allowed to stand for four hours. The volume of undissolved sample is determined by adding saturated salt solution to bring the supernatant material into the graduated neck of the flask.

(*d*) Detection of Pyridine Bases in Denatured Alcohol and in other Solutions

Pyridine bases can readily be detected in denatured alcohol by adding a solution of mercuric potassium iodide,[1] which produces a yellow crystalline precipitate even in dilute solutions. The sample

[1] Tallantyre, *J. Soc. Chem. Ind.*, 1930, **49**, 466 T.

of alcohol is evaporated to dryness with a little sulphuric acid, the residue distilled with aqueous sodium hydroxide and the distillate treated with the reagent. To confirm the presence of pyridine the precipitate is filtered off, washed and heated with potassium hydroxide solution, when the characteristic smell of pyridine is observed.

Tallantyre reviews various methods for the detection and determination of pyridine. The sensitivity of various tests is given as follows :—

Reagent.	Sensitivity— 1 part of pyridine in :—
5 per cent. solution of mercuric chloride .	1,000 parts of solution
Iodine in potassium iodide solution [1] .	200,000 ,, ,,
5 per cent. solution of phosphotungstic acid	50,000 ,, ,,
5 per cent. solution of silicotungstic acid .	8,000 ,, ,,
Cyanogen bromide and aniline . . .	350,000 ,, ,,
Copper sulphate and ammonium thiocyanate	10,000 ,, ,,
Bismuth ammonium citrate (Dragendorff's reagent)	4,000 ,, ,,

Most of these tests are best performed in neutral or very faintly acid solution. The cyanogen bromide and aniline test and the copper sulphate-ammonium thiocyanate test are practically specific for pyridine ; the other tests apply also to pyridine analogues, which are more sensitive than the pyridine. The cyanogen bromide-aniline test, described by Lehner,[2] is very sensitive. If a few drops of aniline are added to a pyridine solution containing water and a trace of freshly prepared cyanogen bromide is added, a bright yellow colour immediately develops and later a reddish-brown precipitate is formed. Ammonia, quinoline and pyrrole are unaffected by this test, but any ammonia present in the solution to be tested must first be neutralized ; if iron is present, this must be removed before the test is performed. Cyanogen bromide is not readily prepared, but a solution of cyanogen bromide in water will suffice. This is prepared by the addition of 3 to 4 volumes of saturated bromine water to 1 volume of a freshly made 5 per cent. solution of potassium cyanide ; the freshly prepared solution should have no yellow colour due to an excess of bromine and will not keep long. The precipitate is due to the formation of the reddish-brown dyestuff, 2.anilinodihydropyridinium phenyl bromide [3] (m.p. 162°).

$$C_5H_5N + CNBr + 2NH_2C_6H_5 = NHC_6H_5 . C_5H_5NHC_6H_5Br + CN . NH_2.$$

(e) Quantitative Estimation of Pyridine Bases

Schulze [4] recommends ferric chloride as an indicator when titrating pyridine bases volumetrically, and states that all other indicators are

[1] Harvey and Sparks, *J. Soc. Chem. Ind.*, 1918, **37**, 41 T.
[2] *Chem.-Ztg.*, 1922, **46**, 877 ; *cf.* Goris and Larsonneau, *Bull. Sci. pharm.*, 1922, **28**, 497.
[3] Koenig, *J. pr. Chem.*, 1904 (ii.), **70**, 19.
[4] *Ber.*, 1887, **20**, 3391.

inapplicable. He dissolves 5 ml. of the basic mixture in 100 ml. of water and adds to the solution 1 ml. of 5 per cent. ferric chloride solution which causes the precipitation of flocculent ferric hydroxide. Normal sulphuric acid is then added until the precipitate just disappears and the liquid becomes perfectly clear; commercial samples require 12 to 13 ml. of the acid. The acid should be added, drop by drop, towards the end of the titration at intervals of one-half to one minute. Tallantyre [1] recommends the use of Ladd's method [2] for the titration of pyridine and pyridine bases employing methyl orange and phenolphthalein. When distillation of the sample is necessary, as in the estimation of pyridine in ammoniacal liquor, the degree of alkalinity of the solution is important. Houghton [3] recommends that the solution be rendered neutral or just alkaline to methyl orange previous to distillation; other authors suggest that the solution be made considerably alkaline. By the first procedure the bases are only partially freed; if the mixture is too alkaline, ammonia, which is usually present, may come over in too great an amount to be destroyed by the sodium hypobromite generally used for this purpose.

Prideaux [4] recommends the addition of normal sulphuric acid and sodium citrate prior to distillation. Tallantyre, however, states that the simplest procedure is to add sodium hydroxide solution cautiously before distillation until the solution shows just a faint pink colour with phenolphthalein indicator, that is a *p*H value of about 10. On distillation all the bases readily pass over together with only a trace of ammonia which is readily decomposed by the sodium hypobromite. The sodium hypobromite solution is not very stable and should be freshly prepared. The bases are absorbed in excess of *N*/10 acid, and the quantity of pyridine bases calculated from the back titration of the acid used with *N*/10 sodium hydroxide solution. 1 ml. of *N*/10 acid corresponds to 0·0079 g. of pyridine; the factor for the conversion of the bases (calculated as pyridine) into commercial pyridine bases is usually about 0·75. Milbauer and Stanek [5] recommend extraction of the bases, using sodium bicarbonate and ether, but the extraction is difficult. Tallantyre proposed the use of pure common salt and benzene for this purpose. The method is conveniently applied to the estimation of pyridine bases in ammoniacal liquor in the following manner:—

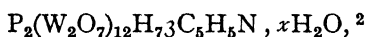
80 g. of pure salt is dissolved in 250 ml. of the sample of liquor, the solution filtered, and shaken in turn with 150 ml., 100 ml. and 100 ml. of benzene. The separated and united benzene extracts are washed with 20 ml. of concentrated salt solution or treated with anhydrous sodium sulphate. The bases are then removed from the

[1] *Loc. cit.* [2] *Ind. Eng. Chem.*, 1919, **11**, 552. [3] *Ibid.*, 1909, **1**, 668.
[4] *Trans. Faraday Soc.*, 1919, **15**, 137. [5] *Z. anal. Chem.*, 1904, **43**, 215.

washed or dried benzene with 25 ml. of *N*/2 sulphuric acid solution, the residues being twice washed with 15 ml. lots of water. The acid solutions and washings are finally titrated with *N*/2 sodium hydroxide solution, using methyl orange and phenolphthalein in the usual way.

The estimation of pyridine by the iodine method[1] is satisfactory only when the solution is clear; otherwise the end-point is indefinite and the precipitate, owing to its varying composition, cannot be weighed. A 5 per cent. solution of either phosphotungstic acid or phosphomolybdic acid may be used for pyridine base determinations. The former, which is the better reagent, should be used only in slight excess and the solution should contain about 1 per cent. of mineral acid with no large amount of salts. Ammonia should be removed prior to the use of the reagent.

The precipitate, which approximates in composition to

$$P_2(W_2O_7)_{12}H_7 3C_5H_5N , xH_2O,$$ [2]

gives, on ignition, a residue of phosphotungstic acid oxide ($P_2(W_2O_7)_{12}H_7$); the weight of the residue is multiplied by the conversion factor 0·041 to give the weight of pyridine in the sample. A second gravimetric method[3] involves the use of silicotungstic acid, a residue of silicotungstic oxide ($SiO_2 , 12WO_3$) being obtained; the conversion factor is 0·12.

Malatesta and Germain[4] precipitate the pyridine in alcoholic solutions with an alcoholic solution of cadmium chloride, and estimate the pyridine by the back titration of the unused cadmium chloride solution with *N*/10 silver nitrate solution; the concentration of the alcohol must be at least 90 per cent. If the pyridine is estimated gravimetrically the formula for the precipitated double compound must be accepted as $CdCl_2 . C_5H_5N$.

VIII. HEAVY OILS

Heavy oils comprise not only the higher boiling fractions of coal tar, but also manufactured residual oils containing small proportions of low-boiling constituents. The greater part of the output is used for the impregnation of timber for preservative purposes. Large quantities are also used as fuel oil for heating and for hydrogenation, as a wash oil for the stripping of coal gas and in the manufacture of prepared tar. Heavy residual oils containing considerable quantities

[1] Harvey and Sparks, *J. Soc. Chem. Ind.*, 1918, **37**, 41 T.

[2] *Cf.* Heiduschka and Wolff, *Schweiz. Apoth.-Ztg.*, 1920, **58**, 213.

[3] *Ibid.*; *Z. angew. Chem.*, 1924, **37**, 89.

[4] *Boll. Chim. farm.*, 1913, **53**, 225; *Annali. Chim. Appl.*, 1914, **2**, 277; *Chem. Zentr.*, 1914, ii. 952.

of crystalline substances are used for the manufacture of lampblack. Anthracene oil is the raw material for the production of carbolineum, and, in Germany, for the preparation of substitutes for heavy mineral oil products.

(a) Creosote Oil

1. **Properties.**—The requirements of the quality of creosote oil for timber preservation vary according to specification. In Germany the different railway and telegraph companies in the separate States have issued specifications; the general specification issued in 1932 by the Central German Railway Bureau is included in the table which follows. In America the creosote users, as represented, for example, by the American Wood Preservers' Association (A.W.P.A.) and the American Railway Engineering Association (A.R.E.A.), issue standard specifications and tests, which latter are uniform with those of the American Society for Testing Materials (A.S.T.M.); other specifications are issued by individual users, such as the different telegraph and telephone companies. A specification [1] has been developed by co-operation between the European producing countries and the Scandinavian consuming countries; its characteristic features are closely connected with the conditions of use in these countries. A similar specification [2] was later developed primarily for use in connection with the supply of creosote oil to the Balkan countries. Both these specifications incorporate tests which are variously based on American, Continental and British methods of examination. In England there is a British Standard specification [3] with tests based on those in *Standard Methods*; the specification is very widely used by British consumers of creosote taken in bulk for timber preservation. The Australian specification is closely in line with the British, while a South African specification is at present in draft form.

Creosote oil is in increasing commercial demand as a fuel oil and a British Standard specification [4] is available; the tests used for determining compliance with the specification are again those of *Standard Methods*; they cover a somewhat different range of properties from those used in the examination of creosote oil for timber preservation. An attempt to develop an alternative British Standard specification for a creosote fuel oil having a lower fluidity point than that represented by *B.S.* 503 proved abortive; the present specification assumes the availability of a measure of heating facilities to maintain complete fluidity in extreme weather conditions.

[1] Scandinavian Specification and Methods of Test for Coal Tar Creosote Oil as used for the Impregnation of Wood, 1937.

[2] Budapest Specification and Methods of Test for Coal Tar Creosote Oil for the Impregnation of Wood, 1938.

[3] *British Standards Institution, B.S.* 144, 1936.

[4] *B.S.*, 503, 1933.

Details of the various Standard Specifications enumerated on preceding page are as follows :—

Description.	Scandinavian Specification for Creosote Oil.	Budapest Specification for Creosote Oil.
	Oil from coal tar other than low-temperature tar.	Oil from coal tar other than low-temperature tar.
Specific gravity S38°/4°	1·025 to 1·135	1·025 to 1·135
Water content, per cent. by volume	Max. 1	Max. 2
Distillation	100 g. to yield :— Up to 210°—max. 4 per cent. (including water) Up to 235°—max. 20 per cent. (including water)	100 g. to yield :— Up to 200°—max. 6 per cent. (including water) Up to 235°—max. 25 per cent. (including water)
Tar acids, per cent. by volume	5 to 9	3 to 9
Fluidity	No solids at 35°	No solids at 38°
Insoluble matter (in benzole), per cent.	Max. 0·5	Max. 0·5
Sample	Representative and not less than 1 litre	Representative and not less than 1 litre

Specifications for Creosote Oil

	A.W.P.A. Standard Specification.			German Specification Central Railway Bureau.
	Grade I.	Grade II.	Grade III.	
Nature of oil	A pure coal-tar distillate.			A pure coal-tar distillate.
Specific gravity	1·03 at 38°/15·5°.			Between 1·04 and 1·15 at 20°.
Distillation	Up to 210°— Not more than 5 per cent. Up to 235°— Not more than 25 per cent.	Not more than 8 per cent. Not more than 35 per cent.	Not more than 10 per cent. Not more than 40 per cent.	Up to 150°, not more than 3 per cent. by volume ; up to 200°, not more than 10 per cent. ; up to 235°, not more than 20 per cent. by volume.
Acid constituents	...			Soluble in sodium hydroxide solution (sp. gr. 1·15) at 15° : at least 5 per cent. by volume.
Water content	Not more than 3 per cent. by volume.			Not more than 1 per cent. by volume.
Solid hydrocarbons Insoluble matter	Not more than 0·5 per cent. of matter insoluble in benzole, and not more than 2 per cent. of coke residue.			Oil must be transparent at 30° and remain clear when mixed with an equal volume of crystallizable benzene. Two drops of the oil and also of the benzene mixture must not leave more than a trace of undissolved matter when placed on a filter paper.

British Standard Specifications for Creosote Oil for Wood Preservation.

	Grade A.	Grade A2.	Grade B.
Nature of oil	A distillate of coal tar, free from any admixture of petroleum or similar oils		
Specific gravity (compared with water at 20°)	Not lower than 1·010, nor higher than 1·065 at 38° (100° F.)	Not lower than 0·995, nor higher than 1·065 at 38° (100° F.) If creosote from low-temperature tar, not lower than 0·935, nor higher than 1·065 at 38° (100° F.)	Not lower than 0·995, nor higher than 1·065 at 38° (100° F.) If creosote from blast furnace tar, not lower than 0·935, nor higher than 1·065 at 38° (100° F.)
Fluidity	To be completely fluid on slow warming to 38° (100° F.) and on cooling remain completely fluid after standing 2 hours at 32° (90° F.). If required for brush application, as above, but on cooling remain completely fluid after standing 2 hours at 15·5° (60° F.)		
Water content	Not more than 3 per cent.		
Distillation	100 g. dry material at 38° to give :— 205° not exceeding 6 g. 230° ,, ,, 40 g. 315° ,, ,, 78 g. Residue—soft and not sticky	100 g. dry material at 38° to give :— 205° not exceeding 6 g. 230° ,, ,, 40 g. 315° ,, ,, 85 g. Residue—soft and not sticky	100 g. dry material at 38° to give :— 205° not exceeding 6 g. 230° ,, ,, 40 g. 315° ,, ,, 85 g. Residue—soft and not sticky
Tar phenols	At least 5 per cent. by volume		
Matter insoluble in benzole	Not more than 0·4 per cent. by weight		
Representative sample	Not less than 1 quart		

The tests are outlined below in the order in which they are treated in *Standard Methods*, those relating to viscosity, flash-point, ash and calorific value being applicable in particular to creosotes intended for use as fuel oil ; the distillation test, the test for residue, and the determination of phenols are characteristic of specifications for creosote oil intended for timber preservation ; the remaining tests—for sp. gr., water, matter insoluble in benzole and fluidity—are applied equally to oils required for use as fuel or in timber preservation though, of course, the specification limits may differ.

Certain of the tests are required in the examination of creosotes intended for use as wash oil in the scrubbing of town gas, or for use in the manufacture of horticultural preparations, disinfectants and so on.

Any samples which show signs of deposition of soluble solid constituents, notably naphthalene, must be warmed gently until these are just dissolved, and portions taken for test from the warm, thoroughly mixed sample.

2. **Specific Gravity.**—In Great Britain the sp. gr. (or the density if that be required instead) is determined by any one of the recognized Standard Methods ; the bottle method should be used for preference and in case of dispute. The basis on which the result is to be reported must be borne in mind : *B.S.* 503, 1933, for creosote fuel oil gives an (upper) limit of sp. gr. in terms of $S_{38° C./38° C.}$; *B.S.* 144, 1936, for creosote for timber preservation is based on limits for $S_{38° C./20° C.}$ (this dissimilarity in specifications from the same source arises simply from the fact that the one specification has not been revised as recently as the other) ; the American specifications give limits for $S_{38° C./15·5° C.}$; the Scandinavian and Budapest specifications for $S_{38° C./4° C.}$ (*i.e.* in effect for density in g./ml. at 38° C.) ; and the German specification is based on limits for $S_{20° C./20° C.}$

The American (A.S.T.M.) Standard Method [1] involves the use of standard hydrometers of specified construction and dimensions, with ranges 0·90 to 1·00, 1·07 to 1·15 and 1·15 to 1·23 and of a glass cylindrical container of standard dimensions. If the oil is sufficiently fluid at 38°, the sp. gr. is ascertained at that temperature ; if a higher temperature is necessary to ensure fluidity, the sp. gr. is ascertained at such higher temperature and a correction of 0·0008 added to the observed value for each Centigrade degree by which the working temperature exceeds 38°. In Germany the sp. gr. is also ascertained by hydrometer, but at a temperature of 20° ; if a temperature in excess of 20° is necessary, a correction of 0·0008 is added for each Centigrade degree above 20°.

3. **Water.**—The Dean and Stark apparatus is used after the manner of the tests on other coal tar products as previously described ; 100 ml.

[1] D 368-33, *Amer. Soc. Testing Materials Standards*, 1936, ii, 548.

of sample is tested and 100 ml. of solvent naphtha is added to facilitate distillation. Modern specifications are becoming increasingly stringent in regard to the water content and for this reason: (*a*) a separate determination by the Dean and Stark method is obligatory in the case of many samples, which contain limited amounts of water, the former procedure of determining the water in the course of the distillation test being unsatisfactory as standard technique in such circumstances; and (*b*) a special form of the receiver in the Dean and Stark apparatus is available (see p. 443) for use with samples containing 1·5 per cent. or less of water.

According to the American Society for Testing Materials Standards, the method described on p. 139 for the determination of water in tar may be employed. Alternatively the metal still shown in Fig. 29, p. 140, may be used with a connecting tube and a copper trough condenser with a straight-walled glass tube, the distillate being collected in a special separating funnel of 120 ml. capacity. The lower portion of the separating funnel is drawn out in the form of a burette which is graduated in 0·2 ml. An American Society for Testing Materials High Distillation standard thermometer of range 0° to 400° is used. 200 ml. of the sample of creosote oil is distilled and distillation is continued until a vapour temperature of 205° is indicated by the thermometer, the bulb of which is opposite the offtake of the connecting tube. The volume of water is noted when a clear separation of water and oil in the separating funnel has occurred.

4. **Distillation.**—At present the British practice, as evidenced by *Standard Methods* and the comparatively recently revised British Standard specification, is to use one of the series of British Standard distillation flasks, air condenser and draught screen, with a thermometer from the standard series (0° to 400° C. in whole degrees); tared 25 ml. and 50 ml. Crow receivers are used to collect the distillate. This assembly is in marked contrast in most respects with the American, while the latter *in toto* or in principle has been adopted in most of the other specifications for creosote. There is a growing body of opinion that the American apparatus should be adopted in connection with the British specification, though that view is largely prompted by a desire for co-ordination rather than that the American apparatus has any intrinsic merits.

With the apparatus described briefly above, 100 g. of dried sample is tested. This dried sample is obtained by distilling about 120 g. from a side arm flask through an efficient condenser until all water has come over; the distillate is collected in a small separating funnel and, when the water has separated, the oily layer is returned to the side arm flask; the contents of this flask are thoroughly mixed and the 100 g. weighed therefrom directly into the standard distillation flask used in the distillation test proper.

Distillation is carried out at the rate of 5 ml. per minute and any test in which this rate is departed from by more than 0·5 ml. per minute after the first 5 ml. have collected must be rejected, a fresh test being started on another 100 g. of dried material. The receiver is changed at the specified temperatures without stopping the distillation except at the final specified temperature. Temperature corrections for barometric pressure are applied (see p. 135).

The American Society for Testing Materials method[1] employs 100 g.$\pm$0·1 g. of the sample, which need not be dehydrated previously if the water present does not exceed 2·0 per cent. Distillation is carried out at a specified and uniform rate from a round-bottomed flask through a glass air condenser into tared 50 to 100 ml. Erlenmeyer flasks. The dimensions of the flask and condenser are closely specified as well as the manner of conducting the distillation, and a standard American Society for Testing Materials High Distillation thermometer of 0° to 400° range is used. The fractions usually reported comprise: up to 170°, 170° to 235°, 235° to 270°, 270° to 300° and residue. The sp. gr. of the fractions is determined by the tentative method of test for the determination of sp. gr. 38°/15·5°, of creosote fractions.[2] In Germany it is customary to use a tubular glass retort of about 250 ml. capacity, the neck of which is attached to an adapter bent at an obtuse angle. The retort is heated on a wire gauze and the distillate collected in a 100 ml. cylinder at the rate of about 120 drops per minute. The retort is charged with 100 ml. of the oil by measuring off 102 ml. and pouring it in through a small funnel; the 2 ml. is about the amount remaining on the sides of the cylinder and the funnel. The volume of the distillate is read off at the specified temperature without interrupting the distillation. When the temperature of 235° is reached the burner is temporarily removed, the thermometer replaced by a good cork, and the distillation continued until 85 to 90 per cent. of the oil has been collected in the cylinder.

5. **Phenols.**—The principle of the Standard Method for the determination of phenols is that of extraction with caustic soda solution, removal of neutral oils and pyridine bases by boiling, liberation of the phenols by acidification and measurement of the volume of phenols. The test is applied to the distillate to 350° C. in the distillation test if the amount of total phenols is required, but it should be noted that, for example, the British Standard specification for creosote oil for timber preservation is only concerned with the phenols in the fraction to 315° C.

The volume of distillate is noted and the distillate transferred to a

[1] D 246-33, *Amer. Soc. Testing Materials Standards*, 1936, ii., 542.

[2] D 368-33, *ibid.*, p. 548.

stoppered separating funnel, warming if necessary to maintain complete fluidity. The method proceeds on lines described formerly (*e.g.* p. 178), but the following points may be noted : (*a*) phenols-free naphtha may be added if necessary to assist the separation of the caustic soda extract from the washed oil layer ; (*b*) the phenols-free oil may have to be reserved for examination for solid hydrocarbons—see section 6 below ; (*c*) the Standard Method prescribes modifications in the procedure to cope with samples containing particularly low and excessively high amounts of phenols.

It is the practice in Germany to heat the oil obtained by distillation with 100 ml. of a solution of sodium hydroxide of sp. gr. 1·15, which has been saturated with common salt to facilitate the separation of the oil, and which has been placed in a stoppered cylinder of 250 ml. capacity. The oily distillate is transferred from the receiver to the cylinder, 25 ml. of pure benzene being used to wash out the receiver. After shaking thoroughly the cylinder is allowed to stand for about an hour, and the increase in volume of the lower aqueous layer is read off in volume percentage.

6. **Solid Hydrocarbons.**—Normally, the solid hydrocarbons are determined by examination of the sample as received, but certain sections of the market demand a determination on the phenols-free material, in which case the washed material from the test for phenols is used ; 50 g. is taken for test in any event, and it is customary to determine the solids deposited at 15·5° C. by subjecting that quantity to that temperature for four hours with occasional stirring. The liquid, initially completely fluid, is seeded with a crystal of naphthalene as soon as the temperature reaches 15·5° C., and at the end of the four-hour period the material is transferred to a cold Buchner funnel fitted with a rapid filter paper. The oil is removed rapidly by means of suction and the residue pressed in a hand screw-press between sheets of blotting paper. The oily margins are removed and separately pressed. The combined pressed residue is weighed. Some purchasers require the determination to be carried out at a temperature other than 15·5° C., frequently lower, even down to 0° C. for very special purposes. It should be noted that the result includes any insoluble matter present in the material tested ; this may be important when testing a borderline sample though the text of the relevant specification would have to be consulted before it could be said that the content of insoluble matter could legitimately be deducted.

7. **Insoluble Matter.**—In this test *Standard Methods* (the more recently revised publication) differs from the requirements of the British Standard specifications and anticipates the probable course of amendment in any future revision of the latter, by using toluole instead of benzole as the solvent. Some 20 g. of the sample is dissolved in

about four times the volume of 90's toluole ; the solution is filtered and the residue washed with more of the toluole until the filtrate evaporates without leaving residue. Drying and weighing follow, in line with the procedure used in corresponding tests on other tar products (see for example p. 408), the particular feature of the test as here applied being that the toluole need not be heated.

In Germany and in America benzene is also used as the solvent. In the former instance 20 ml. of the well-shaken and completely liquid oil at 30° is shaken thoroughly in a measuring cylinder with an equal volume of pure crystallizable benzene. The solution should not be perceptibly turbid and should not leave a distinct black spot on filter paper. The original oil should also satisfy these requirements at 30°. In America continuous extraction with the vapours of the boiling solvent in an extractor of a suitable form is specified. 50 ml. of pure benzene is added to 10 g. of the dry oil contained in a 100 ml. beaker, and the whole at once transferred to a tar filter cup or thimble. The filter cups may be made of two thicknesses of hardened filter paper (Whatman No. 5), 15 cm. in diameter or a flat-bottomed alundum thimble (30×80 R.A. 98) may be used. The beaker is washed out with a sufficient quantity of benzene through the filter cup, the filtrate passing into the extractor. The solvent is then boiled and extraction continued until the descending solvent is practically colourless. The filter cup is removed, dried in a steam oven, cooled in a desiccator and weighed to within 0·5 mg.

8. **Ash.**—The Standard Method is to distil an accurately weighed amount (about 200 g.) until a small residue remains, but without coke formation. The amount of residue is obtained by difference and about half is weighed into a crucible. The crucible is heated cautiously at first and finally is ignited until all combustible matter is burnt, when the crucible is allowed to cool and is then weighed. The ash is obtained by difference and calculated as a percentage on the sample.

9. **Coke Residue.**—The method devised by Conradson [1] for use particularly in connection with petroleum products has been adopted in connection with the testing of creosote oil. The apparatus is shown in Fig. 50. A portion of the sample is burnt under thoroughly controlled conditions in the crucible A and the coke remaining in the crucible at the end of the test is weighed. The results must be interpreted with caution and in proper relation to the results of other tests and to the purpose for which the creosote oil is intended. In America the determination of the coke residue [2] is carried out in the electric tube furnace shown in Fig. 51.

[1] *8th Int. Con. App. Chem.*, 1912, 1, Section I, p. 131.

[2] D 168-30, *Amer. Soc. Testing Materials Standards*, 1936, ii., 553.

1. g. ± 0·1 g. of the residue is weighed into the platinum capsule crucible, which has a capacity of 25 to 30 ml. and which weighs with the cover 25 to 30 g. The tightly-fitting cover is provided centrally with a hole of 2 mm. diameter. The temperature of the furnace is raised to 950° ± 20°, and the covered crucible, containing the weighed residue, heated therein for exactly seven minutes. It is then removed, cooled and weighed. Alternatively, a fully aerated Bunsen or Meker burner may be used for heating the crucible, provided that the required temperature is attained inside the crucible as shown by the fusion of crystals of potassium chromate in the crucible when heated under the conditions of the test. The percentage of coke in the residue as obtained by experiment is calculated to a percentage of the total oil by multiplying by $\frac{A}{100}$ where A is the percentage residue from the oil distilled to 355°.

Fig. 50.—Coke Residue on Evaporation of Creosote Oil—Assembled Apparatus.

10. **Fluidity.** — The usual basis of fluidity clauses in creosote oil specifications is the requirement that the oil shall be completely fluid for a specified period of time at a specified temperature. Occasionally the temperature of first appearance of soluble solid matter from a cooling sample is required. The Standard Methods are respectively as follows :—

(*a*) Fluidity at a Specified Temperature : About 50 g. of the sample is taken in a 100 ml. conical flask. A standard thermometer of appropriate range is fitted by means of a cork so that its bulb is immersed in the oil, and, with the oil initially completely fluid, the flask and contents are slowly cooled to the temperature of test. The temperature of test is maintained for two hours ; the flask is then withdrawn and rotated slowly in a horizontal position, examining for separation of soluble solid matter which if present will adhere to the side of the flask or float on the liquid surface. If necessary, in case of doubt, the contents of the flask are filtered rapidly through a

Buchner funnel fitted with filter paper and operating under vacuum; the paper is examined for soluble solid matter.

(*b*) Temperature of Deposition: The general arrangements are as under (*a*) above, but the assembled apparatus is placed in a bath at about 10° C. below the expected deposition-point. It is frequently

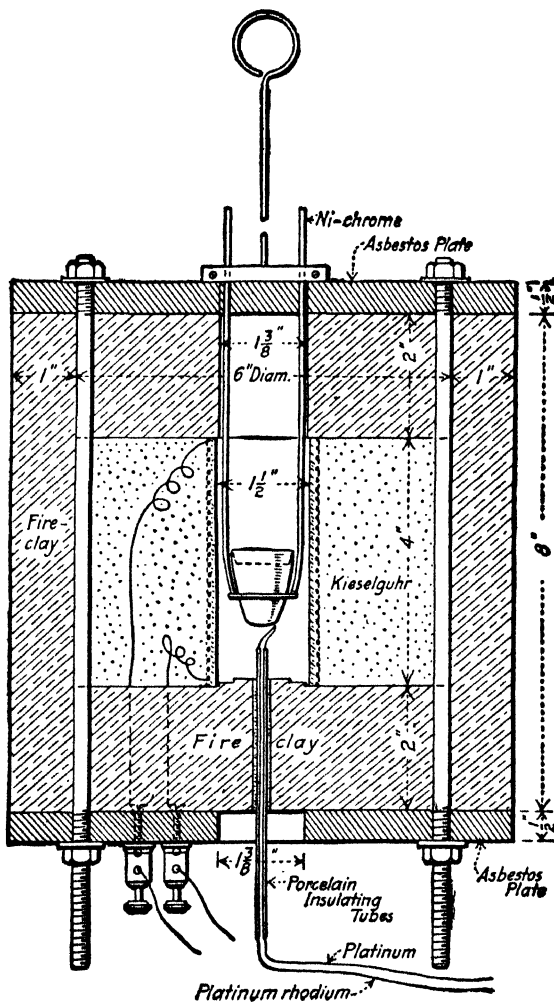



FIG. 51.

rotated and withdrawn at intervals for examination for separation of soluble solid matter; the temperature at which such matter first separates is reported.

11. **Flash-point.**—A Pensky-Martens closed tester to the specification of the Institute of Petroleum [1] is used. The test is carried out

[1] *Standard Methods for Testing Petroleum and its Products*, 1935, p. 99.

on the dried sample, obtained by dehydration of powdered plaster of Paris at 50° C. for seven hours with hourly shaking. The cup of the instrument is filled with the dried sample to the filling mark, the apparatus assembled and the test flame adjusted to the proper size. The temperature is raised at a rate of 9 to 10° F. per minute, the stirrer is rotated at a rate of about sixty revolutions per minute and test flame applications are made at multiples of 2° F., starting at a temperature at least 50° F. below the expected flash-point; stirring is discontinued during test flame applications. The flash-point is the temperature at the time of the test flame application which causes a distinct flash in the interior of the cup; corrections are made for barometric pressure by adding or subtracting 0·63° F. for each 10 mm. by which the prevailing pressure is below or above 760 mm.

12. **Viscosity.**—A Redwood No. 1 Viscometer to the specification of the Institute of Petroleum [1] is used.

About 200 ml. of sample is heated to within a few degrees of 100° F., the bath of the viscometer is heated to a few degrees above 100° F. and the warmed sample is poured into the oil cup through a fine mesh filter. The temperature of the bath is adjusted until the temperature of the oil in the cup is steady at 100° F., the stirrer in the bath being gently rotated. When the oil reaches the steady temperature, its level is adjusted by allowing oil to flow out until the surface of the oil touches the filling-point. The oil cup cover is slightly warmed and placed in position and the specified flask is placed under the jet of the instrument. The valve is lifted and a stop-watch started at the same time; it is stopped when the oil reaches the 50 ml. graduation mark on the flask. The interval in seconds is reported as the viscosity.

13. **Calorific Value.**—The gross calorific value is determined by the bomb method in terms of 15° C. calories under conditions of constant volume for the products of combustion. The Standard Method is in line with the recognized procedure for such work and little need be said about the details in the circumstances. About 0·8 g. of sample is burnt and if the total sulphur is to be determined (see subsection 14 below) that determination is anticipated when the bomb is opened up after the calorimetric part proper of the method. The example on p. 367 will illustrate the method and the subsequent calculations.

[1] *Standard Methods for Testing Petroleum and its Products*, 1935, p. 161.

Capsule+creosote oil	= 7·6357 g.	Water	= 2,367 g.
Capsule	= 6·7191 g.	Total water value	= 2,800 g.
Creosote oil	= 0·9166 g.	Final temperature of water	= 16·5° C.

Preliminary period.		Chief period.		After period.	
Time.	Temperature.	Time.	Temperature.	Time.	Temperature.
0	1·129	6 (t_1)	1·87	12 (t_7)	4·081
1	1·133	7 (t_2)	3·17	13	4·078
2	1·137	8 (t_3)	3·805	14	4·074
3	1·141	9 (t_4)	4·002	15	4·071
4	1·144	10 (t_5)	4·068	16	4·068
5 (t_0)	1·148	11 (t_6)	4·080	17	4·065

$t = 1{\cdot}139$	$\Sigma_1^{n-1}(t) = 20{\cdot}995$	$t' = 4{\cdot}073$
$v = -0{\cdot}0038$	$\frac{1}{2}(t_0+t_n) = 2{\cdot}615$	$v' = 0{\cdot}0032$
$n = 7$	$23{\cdot}610$	$k = \dfrac{v'-v}{t'-t} = 0{\cdot}00239$
$nt = 7{\cdot}973$	$-nt = -7{\cdot}973$	
$nv = -0{\cdot}0266$	$T = 15{\cdot}637$	$kT = 0{\cdot}0374$

Cooling correction $= nv + kT$
$= -0{\cdot}0266 + 0{\cdot}0374$
$= +0{\cdot}011$ Centigrade degree

0·1 *N* sodium carbonate solution		=	25 ml.
0·1 *N* hydrochloric acid(v_1)		=	14·8 ml.
Barium sulphate		=	0·0541 g.
Combustible sulphur (w)	= 0·0541 × 0·1373	=	0·0074 g.
Correction for nitric acid	$= (25 - v_1 - w/0{\cdot}0016) \times 1{\cdot}43$		
	$= \left\{25 - 14{\cdot}8 - \dfrac{0{\cdot}0074}{0{\cdot}0016}\right\} \times 1{\cdot}43$	=	8 calories
Correction for sulphuric acid	= 0·0074 × 2250	=	17 calories

		° C.
Uncorrected temperature rise ($t_n - t_0$)	=	2·933
Cooling correction	=	+0·011
Calibration correction	=	−0·003
Correction to 15° C. calories	=	nil
Corrected rise	=	2·941
Heat liberated = 2·941 × 2,800	=	8,235 calories
Correction for thread −20; Correction for nitric acid − 8; Correction for sulphuric acid −17	=	−45 calories
Heat from 0·9166 g. of creosote oil	=	8,190 calories
Heat from 1 g. of creosote oil	=	8,935 calories
Calorific value	=	8,935 calories per g.
or, multiplying by 1·8,	=	16,083 B.Th.U. per lb.

Such a result should be rounded off to 16,080 B.Th.U. per lb.

Limits of Accuracy. The results of two consecutive tests should fall within thirty units of each other and the mean of the two readings should be within ±0·2 per cent. of the true value.

14. **Total Sulphur.**—This is determined gravimetrically as barium sulphate in the usual manner, using the washings from the bomb on completion of the determination of the calorific value of the oil.

15. **Float Test.**—In America, one further test is applied to creosote for wood preservation. It is a float test on the residue in the retort at the end of the distillation test. The method is the same as that for the float test on bituminous materials.[1]

(*b*) Fuel Oil

The use of tar as a fuel for internal-combustion and compression-ignition engines is discussed by King and Cawley.[2]

In Germany fuel oil for use in furnace heating is required to have a sp. gr. of 1·02 to 1·08 at 20° and a flash-point (open test) of not less than 65°. The oil should not contain more than 0·5 per cent. of water and must be free from sediment after cooling at 0° for three hours. Any solids which separate *on lengthy storage* (as, for example, naphthalene) must go back into solution on slight warming. The lower heating value of the oil should be about 9000 calories. On distillation up to 270° at least 13 per cent. should distil over. The ash content should not exceed 0·05 per cent., and the coke residue should not be more than 3 per cent.; the content of xylene insoluble material should not exceed 0·2 per cent. A special fuel oil is produced (tiefgekühltes) which is free from sediment after cooling to −7° and maintaining at this temperature for twenty-four hours. Another preparation (the so-called "gestrecktes Heizöl") consists of 80 per cent. of tar oil and 20 per cent. of pitch. It has a flash-point not lower than 75°, and a viscosity exceeding 8° Engler; on maintaining at 8° for two hours it must remain free from sediment and must not contain more than 4 per cent. of free-carbon. The heating value must be at least 8500 calories.

The British Standard specification for creosote for fuel in furnaces [3] requires the following:—

1. The creosote must be essentially a coal-tar distillate and free from admixtures of petroleum or undistilled crude tars. It must be practically free from inorganic acids and completely free from sediment and other impurities likely to choke the burners.
2. The sp. gr. at 38° must not exceed 1·07 (p. 359).
3. The viscosity must not exceed 100 seconds (Redwood No. 1) at 38° F. (p. 366).

[1] D 139-27, *Amer. Soc. Testing Materials Standards*, 1936, ii., 1061, also approved by American Standards Association.

[2] *J. Inst. Fuel*, 1936, **10**, 48.

[3] Extracted by permission from *B.S.* 503, 1933.

4. The water content must not exceed 1 per cent. by volume (p. 359).
5. The material insoluble in benzole must not exceed 0·5 per cent. by weight (p. 362).
6. The creosote must become completely liquid on being slowly warmed to 38° with stirring and, on cooling, remain free from suspended solids after standing for two hours at 32° (p. 364).
7. The flash-point must not be lower than 150° F. (Pensky-Martens closed test) (p. 365).
8. The ash content must not exceed 0·05 per cent. (p. 363).
9. The gross calorific value must be at least 16,000 B.Th.U. per lb. (p. 366).

The tests for these characteristics have been dealt with on the page cited against each.

(*c*) Diesel Oil

In the German market, tar oils for use in Diesel engines must possess the following properties :—

1. The sp. gr. at 20° should be between 1·02 and 1·08.
2. In the distillation test at least 60 per cent. of the oil must distil over below 300°.
3. The flash-point must not be below 65° (open test).
4. The water content must not exceed 0·5 per cent.
5. The coke residue must not exceed 3·0 per cent.
6. The ash content must not exceed 0·02 per cent.
7. The oil must be free from sediment after maintaining at 0° for a period of twenty-four hours.
8. The oil must not contain more than 0·2 per cent. of solid constituents insoluble in xylole.
9. The chlorine content must not exceed 0·02 per cent. The chlorine content is determined as follows :—

50 ml. of the oil is placed in a 100 ml. graduated cylinder provided with a tightly-fitting glass stopper and shaken thoroughly for one minute with 50 ml. of distilled chlorine-free water at a temperature of 60° to 70°. After separation the aqueous layer is filtered through a small folded filter paper. 10 ml. of the filtrate is pipetted off, mixed with 100 ml. of chlorine-free water, 5 ml. of chlorine-free nitric acid and 10 ml. of 5 per cent. silver nitrate solution, and raised to the boil. The precipitate of silver chloride is filtered off, washed with hot water, acidified with a drop of nitric acid, incinerated together with the filter paper, and treated with nitric acid and with hydrochloric acid in the usual manner. The crucible is heated gently until the silver chloride begins to fuse, allowed to cool and weighed. The observed weight multiplied by the factor $\frac{2{\cdot}474}{S}$, where S is the sp. gr. of the oil, gives the chlorine content of the oil as a percentage.

10. The sulphur content should not exceed 0·1 per cent. It may be determined by using a bomb calorimeter.
11. The lower calorific value of the oil should be about 9000 calories.

(*d*) Naphthalene and Benzene Wash Oil

Wash oils are used for the recovery of benzole from coal gas, in particular in the coke-oven industry, and for the purification of town

gas from naphthalene, in the gas industry. Creosote oil is most extensively used for this purpose and numerous specifications of quality have been issued; the following are typical:—

I.*		II.†	
Specific gravity at 60° F. . . .	1·010 to 1·030	Specific gravity .	1·035
Initial boiling-point	Above 200°	Drip-point . .	210° to 220°
Distillation range .	Not less than 70 per cent. nor more than 90 per cent. at 300°	50 per cent. distillate at . . .	250°
		80 per cent. distillate at . . .	300°
Naphthalene .	None should deposit on cooling to 55° F.	Naphthalene . .	Distillate to 300° should not settle out more than 7 per cent. of solid at 45° F.
Tar phenols . .	Immaterial; usually 8 to 9 per cent.	Water . . .	Traces

* Specification, Department of Explosives Supply, Whitehead, *Benzol*, London, 1920, p. 46.
† Walmsley and Morfey's Specification, *ibid.*

The table (p. 371) of comparative data relative to creosotes and creosote fractions for benzole recovery was compiled by Hoffert and Claxton.[1]

According to Hoffert and Claxton,[2] who discuss in detail the recovery of benzole by gas stripping, two important characteristics of creosote oil for this purpose are its distillation range and its composition. Lowering the average boiling-point of a creosote oil increases the absorptive capacity, provided the relative proportions of the various types of constituents remain unaltered. The chief constituents of a creosote that influence its absorptive capacity are the tar phenols and naphthalene. Tar phenols alone have an appreciably lower absorptive capacity than creosotes. Low-boiling tar phenols, such as phenol and the cresols, *when present in low concentrations*, are practically without influence on the absorptive capacity of a wash oil; high-boiling tar phenols tend to lower the absorptive capacity. When present in appreciable amounts, both low- and high-boiling tar phenols tend to lower the absorptive capacity. Naphthalene in a wash oil, in cases where naphthalene in stripped gas is of little consequence, is advantageous. In view of the possible emulsification of the wash oil with water the sp. gr. of the oil must also be taken into consideration in conjunction with its other properties.

Other coal tar oils used for this purpose include anthracene or green oil, and in Germany brown coal or lignite tar oils; tetralin has also

[1] *Motor Benzole, Its Production and Use*, London, 1931, p. 116.
[2] *Ibid.*, 1938, p. 200 *et seq.*

Creosote.	Specific gravity at 20°.	Viscosity at 20°.		Distillation range.				Tar phenols (per cent. by volume).	Naphthalene by picrate method (per cent. by weight).	Volatility loss to gas at 20°.		Absorptive capacity at 20°.	
		Redwood seconds.	Absolute units.	0·0	5·0	50·0	95·0			G. per cu. metre at 20° and 760 mm.	Gall. per 10,000 cu. ft. at 20° and 760 mm.	G. per 100 g. of solution.	Volume per 100 volumes absorbent.
				Per cent. by volume distillate at °C.									
Fraction 205° to 265°, free from tar phenols	0·9535	30·5	0·0230	204·5	207·0	222·0	253·0	nil	35·5 (15·0°) *	2·8	0·183	4·55	5·15
Chlorinated creosote fraction, 200° to 300°	0·9760	31·0	0·0255	200·0	210·5	238·0	288·0	nil	25·0 (15·0°)	2·15	0·137	4·30	5·00
Fraction 210° to 280°, containing tar phenols	1·0275	39·4	0·0570	210·0	211·0	224·0	264·0	33·0	40·0 (0°)	1·0	0·063	3·60	4·25
Fraction 210° to 280°, free from tar phenols	1·0055	31·3	0·0274	210·0	212·0	233·5	263·0	nil	54·5 (0°)	2·2	0·137	4·25	5·05
Light creosote, 200° to 300° . . .	1·0135	34·6	0·0400	200·0	207·0	229·0	300·0	17·5	35·0 (15·0°)	1·9	0·117	3·95	4·75
Creosote, 220° to 350°, free from tar phenols	1·0015	35·6	0·0430	219·0	227·0	264·5	334·0	nil	14·0 (0°)	1·65	0·100	3·80	4·50
Creosote, containing 8 per cent. by weight of added naphthalene .	1·0090	35·2	0·0415	...	...	...	...	nil	22·0 (18·0°)	...	...	3·95	4·70
Medium creosote .	1·0310	37·6	0·0510	200·0	208·0	245·0	90 per cent. (350)	20·0	0·2 (0°)	2·0	0·121	3·60	4·35
Blast furnace creosote (washed) . . .	0·9350	39·8	0·0530	210·0	220·0	269·5	340·0	4·0	0·2	1·0	0·067	3·65	4·05
Blast furnace creosote, containing 17·4 per cent. by weight of added naphthalene .	0·9510	37·3	0·0460	...	...	...	...	...	17·6 (16·0°)	...	...	4·00	4·50
Cresol . . .	1·039	65·4	0·1345	(197 to 200)				100	nil	0·77	0·045	2·80	3·40

* Temperatures of cooling for naphthalene separation.

been used to a small extent. The properties desired in these wash oils are indicated in the following specifications :—

	Anthracene oil.*		Heavy lignite † tar oil.
Specific gravity	1·08 to 1·10		0·91 (20°)
Drip-point	220°		230°
25 to 30 per cent. distillate (by volume) at	300°	2 per cent. distillate (by volume) at	250°
75 to 80 per cent. distillate (by volume) at	370°	20 per cent. distillate (by volume) at	200°
Anthracene (b.p. 340°)	Not more than 2 per cent.	98 per cent. distillate (by volume) at	400°
		Solidification point	−4°

* Pooley, J., *Gas Lighting*, 1916, **133**, 689.
† Thau, *Gas- u. Wasserfach*, 1924, **67**, 163; Glückauf, *ibid.*, 1925, **61**, 117; Stumpf, *ibid.*, 1924, **67**, 515 Trutnovsky, *Teer u. Bitumen*, 1929, **27**, 477.

Besides the methods for the examination of wash oil which have already been described on p. 359 *et seq.*, an additional test is the determination of the absorptive capacity of the oil. According to Hoffert and Claxton [1] this is determined as follows :—

A stream of dry air or nitrogen is brought into intimate contact with a solution of benzene in the wash oil, maintained at a constant temperature, and the loss in weight of the solution is determined. From the loss in weight the concentration of benzene vapour in the air or nitrogen after passage through the solution can be calculated, and the partial pressure is then derived from the total pressure of the benzene vapour-air or nitrogen mixture. For a complete description of the apparatus used, the experimental method and the nature of the calculation involved the authors' original communication should be consulted.

(*e*) Carbolineum and Tar Insecticides

(1) **Properties.**—Carbolineum is the name given to an oil which is used for painting on wood to protect it from rotting and as a winter wash for the destruction of insect eggs on fruit trees. It consists of heavy coal tar oil or a solution of an emulsifier in the tar oil prepared from the so-called green oil (filtered anthracene oil) to which small quantities of other wood preservatives are sometimes added, such as zinc chloride or resins (colophony). A " stock-emulsion " type in which the oil is already present in an emulsified form and a " tar oil-sulphonated oil mixture," commonly called a two-solution wash, and requiring the

[1] *Motor Benzole, Its Production and Use*, London, 1938, p. 829 ; *Rept. Joint Benzole Res. Comm.*, 1926, p. 134.

addition of alkali to the oil-water mixture to give the correct emulsion, are also generally marketed. Carbolineum is usually of a brown colour, but is occasionally specially coloured by the addition of oil-soluble dyestuffs. " Carbolineum Avenarius " (trade mark) is a product manufactured by the action of chlorine on the oil. Carbolineum is often imitated by substituting other mineral oils, middle and heavy tar oils, and even oil and water-gas tars, which do not, however, exert nearly so powerful a preservative action as anthracene oil. Mallison [1] gives the following information relative to carbolineum :—

The Verkaufsvereinigung für Teererzeugnisse of Essen has the following specification :—

1. The carbolineum must consist only of high-boiling coal tar oils.

2. On distillation in a copper flask up to a temperature of 250°, the volume of distillate obtained must not exceed 10 per cent.

3. The flash-point (open test) must be at least 100°.

4. The sp. gr. at 20° must be between 1·08 and 1·11.

5. The volume of tar phenols soluble in sodium hydroxide solution (sp. gr. 1·15) must not exceed 10 per cent.

6. The oil must be free from sediment on cooling to 15°.

7. On mixing with an equal volume of benzole (" Reinbenzol," Benzolverband),[2] not more than a trace of insoluble matter must separate out. When 2 drops of the carbolineum are poured on to a filter paper the carbolineum must be absorbed ; at most only a trace of solid carbonaceous material must remain.

8. The water content must not exceed 1 per cent.

The specification for carbolineum of the German Reichspost-zentralamt is as follows :—

Sp. gr., at least 1·10 at 20° ; sediment-free at 20° ; free from insoluble matter ; on distillation in a glass retort giving only a trace of distillate at 150° and not more than 4 per cent. up to 250° ; not more than 8 per cent. of tar phenols ; a viscosity of at least 6° Engler at 20° and a flash-point of at least 125° (open test).

(2) **Examination.**—The following are determined :—

a. *Specific gravity.* This is determined by means of the hydrometer, Westphal's balance, or the sp. gr. bottle.

b. *Salts* or sediment at 15° and 20° respectively are determined by maintaining the sample at these temperatures and filtering and weighing in the usual manner.

c. *Boiling range.* This should be ascertained by the Standard Method (p. 360) as for creosote oil ; the nature of the residue is noted as to whether this is oily, crystalline or pitchy. In dealing with high-

[1] *Chemisch-technische Untersuchungsmethoden*, Berl-Lunge, Berlin. 1933, p. 347.
[2] p. 211.

boiling oils separated from tar emulsions a special procedure (*vide infra*) may be advisable.

d. *The Water Content* is determined by the Standard Method.

e. *Tar Phenols* are determined by the Standard Method in the case of carbolineum. With an emulsion the special procedure should be employed.

f. *The Viscosity* of the oil is determined in the United States with the Saybolt viscometer, in England with the Redwood instrument, and in Germany with the Engler viscometer.

g. *Volatility*. No standard method for the determination of volatility has been adopted. Some authorities employ a distillation test,[1] others a loss-by-evaporation test comparable to the standard volatility test adopted by the Institution of Petroleum Technologists.[2]

h. *Ash* is determined in the usual manner.

(3) **Tar-Oil Emulsions.**—For the examination of tar-oil emulsions it is necessary to separate the neutral oil after breaking the emulsion; for this purpose a concentrated solution of sodium hydroxide, followed by extraction with ether after separation, is employed. Martin[3] describes the method as follows:—

50 g. of the stock emulsion, diluted with 500 ml. of water, is shaken in a large separating funnel with 100 ml. of 10 per cent. sodium hydroxide solution. The mixture is then extracted with four or five lots of 200 ml. of methylated ether (sp. gr. 0·730). The combined ether extracts are washed with 1 per cent. sodium hydroxide solution, concentrated on the water-bath and dried with anhydrous sodium sulphate. After twenty-four hours the solution is filtered into a weighed flask, the ether distilled off and the final traces removed by drying for two hours in a steam oven and gently blowing with air; the residual oil is weighed. If the content of tar bases is required, the ether extract is washed with successive amounts of 4 per cent. hydrochloric acid until the acid layer is no longer coloured; the tar bases are extracted from the hydrochloric acid washings with ether after making alkaline with sodium hydroxide solution. The residual oil is used for the determination of boiling range. To determine the tar phenols present in the aqueous sodium hydroxide layer and washings, the ether is first removed by distillation; solid barium hydroxide is added to remove soaps, resin, sulphonated oil or other emulsifying agent; the solution is filtered and acidified, and finally the cooled filtrate extracted with ether. The ether solution after drying over anhydrous sodium sulphate is treated in the same way as the neutral tar-oil solution, and the weight of tar phenols so determined. During the distillation of the separated

[1] Woglum, *Handbook of Citrus Insect Control for* 1930, California Fruit Growers Exchange, Bull. No. 7, 1930.

[2] *Standard Methods of Testing Petroleum and its Products*, London, 1935, p. 184.

[3] *J. Soc. Chem. Ind.*, 1931, 50, 91 T.

neutral oil, particularly with oils boiling above 280°, cracking of the oil may occur and considerably affect the results ; in this case distillation is carried to 260°, the distillate weighed, and the amount of high-boiling oil determined by difference.

Reference should also be made to the methods of analysis of tar disinfectants proposed by Houben [1] for the analysis of fruit-tree carbolineums.

IX. MINERAL OIL AND GREASE SUBSTITUTES

In Germany high-boiling constituents of coal tar furnish the raw material for the manufacture of mineral oil and grease substitutes, the so-called "Teerfettöl." Bruhn [2] gives a comprehensive classification of the properties and application of these products. For particulars of methods of analysis this account should be consulted as well as the volume of the present work dealing with the examination of fats and greases.

X. PREPARED TAR

(a) Properties

The term "Prepared Tar" may be considered to cover a variety of products which differ considerably in composition and physical properties according to the method of preparation. Certain "distilled" tars are produced by distilling off the light-boiling constituents, the residue then being a prepared or distilled tar ; in the case of other products the tar constituents, namely the pitch and tar oils, are completely separated by distillation and again mixed in the proportions necessary to give products possessing the special characteristics required in tar preparations for various technical purposes. In the former case the manufacturer is restricted largely by the nature of the various crude tars employed ; with true "prepared" tars, a product is more readily produced with the specified properties. Large quantities of prepared tar are used in the manufacture of roofing felt and similar materials,[3] as roofing tar, and for the preparation of black varnishes. By far the largest amount, so far as Great Britain is concerned, is used for the surfacing of roads. In certain branches of the electrical industry, prepared tar is used as a binding agent in the manufacture of electrode and lighting carbons and as an insulating material. A special quality is used in the steel industry under the name of steelworks tar for the preparation of basic converter linings.

[1] *Nachr. deut. Pflanzenschutzdienst.*, 1930, **10**, 2.
[2] *Stahl. u. Eisen*, 1919, **39**, 402, 469.
[3] *British Standards Institution, B.S.* 747, 1937.

A rust preventative is manufactured by dissolving pitch in tar oils. Finally, prepared tars are used as substitutes for asphalt, and as insulating materials in the asphalt and building industries.

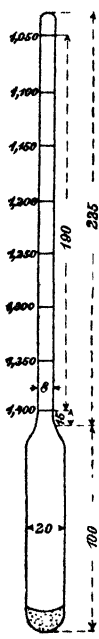
(*b*) General Methods of Examination

Prepared tars are commonly examined for sp. gr., water content, viscosity, the quantity and nature of the liquid constituents, the coking residue and the free carbon content.

1. **Specific Gravity** is determined as described on p. 393.

2. **Water Content** is determined by means of the standard Dean and Stark apparatus by the method described on p. 405.

Fig. 52.

3. **Viscosity.**—For the testing of samples of refined tar for viscosity, a modified type of Redwood viscometer is in use in England, particularly for samples of road tar. In Germany, the Engler viscometer may be used, but, especially in the roofing felt industry, a type of viscometer known as Rütgers is commonly employed. It is described by Mallison.[1] It has a capacity of about 500 ml. and is provided with an orifice of 5·15 mm. diameter which can be closed by means of a wooden rod. The test is usually carried out at 50°, the vessel being filled with the sample of tar at a temperature of 53° to 54° up to a mark which corresponds to a quantity of tar of 475 ml. The temperature is then allowed to fall to 50°, the orifice opened by removing the wooden rod, and the time in seconds required for 300 ml. of the tar to run into a graduated glass measuring vessel is accurately noted. This value ranges from twenty to sixty-five seconds for thin to thick liquid tars respectively. The Rütgers viscometer is specified in the German Standard Specification, D.I.N.-D.V.M. 2137 *Prüfung von Steinkohlenteeren als Dachanstrichstoffe.*[2]

Lunge describes a "tar-tester," Fig. 52, which is made of thick-walled glass, weighs about 39 g., and has a scale of specific gravities from 1·050 to 1·400 on the narrow portion. The instrument is used in the same manner as an ordinary hydrometer, excepting that it is not allowed to sink into the liquid till in stable equilibrium, but only till it reaches a certain point which lies sufficiently below that corresponding to the sp. gr. of the tar; for this purpose the point 1·250 has been chosen as a practical figure. The determinations are made at a definite temperature, usually at 15°, and the tar, as measured, must be brought to within at least

[1] *Chem.-Ztg.*, 1925, **49**, 392; *Teer u. Bitumen*, 1928, **26**, 317.

[2] *Deutscher Normenausschuss*, Berlin, 1933.

half a degree of this temperature, using a standard thermometer. Before the actual determination, the tar must be well mixed by thoroughly stirring up with a wire stirrer. The tar-tester is most conveniently suspended by means of a spring clip, above the cylinder containing the tar. The instrument is first dipped into the tar up to the mark 1·250, withdrawn, and suspended for three minutes by the clip to drain, as there is a difference of several seconds in the rate at which a clean instrument and one covered with tar sinks in the same tar. As it is necessary to take several readings, it is simpler to use an instrument which has been merely drained in this way than to clean it each time. The tester is then held so that its lower end just touches the tar and is allowed to sink by its own weight, the time taken to reach the 1·250 mark being noted by means of a watch with a seconds' hand. It sinks very rapidly until the wide portion is immersed, then more slowly. If the instrument leans to one side and touches the wall of the cylinder, it may be righted by a gentle touch from the side without causing appreciable error, provided that all downward pressure is avoided. Three or four determinations should always be made, the instrument being allowed to drain for two to three minutes between each, and they should agree to within two to three minutes. By allowing the instrument to sink until it comes to rest, a determination of the sp. gr. of the tar may be made at the same time, but it is not so exact as the method described.

4. **Free - Carbon.**—Free - carbon is determined by the method described on p. 407; the determination of the coking residue is described on p. 363.

5. **Volatile Constituents.**—This determination may be made by distilling 1 kg. of the tar under ordinary pressure in a cast-iron 2 litre still fitted with a glass T-piece and thermometer in such a manner that the separate distillates can be collected in weighed glass flasks. Light oils are collected up to 200°, naphthalene oils up to 250°, and heavy oils up to 340°. Generally a medium hard pitch of softening point between 60° and 75° remains in the still, the weight of pitch being obtained by difference. The softening point is determined by the Kraemer and Sarnow method (p. 417), and if this lies above 75° or below 60° the distillation must be repeated, choosing a suitable end-point above 340°, if one below 340° had been employed previously. Decomposition of the tar, denoting the commencement of coking, must be guarded against. The naphthalene oils and heavy oils are examined for their contents of naphthalene and anthracene respectively by cooling in ice-water for thirty minutes, filtering the oils at the pump and drying the separated crystals on a porous tile. The weights give approximately the content of these constituents in the tar in a technically pure state; they may be examined by the methods already described.

(*c*) Roofing Materials

Specifications for prepared tars for the manufacture of roofing materials are given in German Standard Specifications,[1] from which the data which follow are extracted :—

Title of Specification.	D.I.N.-D.V.M. 2122.	D.I.N.-D.V.M. 2136.	D.I.N.-D.V.M. 2138.
Manner of manufacturing the product.	(*a*) By the distillation of coal tar. (*b*) By mixing coal tar pitch with coal tar oils. (*c*) By mixing coal tar pitch with the product of (*a*) or (*b*) (*d*) By the mixing of products (*a*), (*b*) or (*c*) with pure asphaltic-base bitumen; the content of bitumen must not exceed 20 per cent.	(*a*) By the distillation of coal tar. (*b*) By mixing coal tar pitch with coal tar oils. (*c*) By mixing coal tar pitch with the product of (*a*) or (*b*).	(*a*) By the distillation of coal tar. (*b*) By mixing coal tar pitch with coal tar oils. (*c*) By mixing coal tar pitch with the products (*a*) or (*b*).
Nature of product	...	Liquid at 20°; smooth and lustrous.	Solid at 20°; smooth and lustrous.
Water content	Maximum, 1 per cent.	Maximum, 1 per cent.	Maximum, 1 per cent.
Ash content	...	" 1 "	" 1 "
Naphthalene content	Maximum, 2·5 per cent.	" 5 "	" 3 "
Boiling range	Up to 250°; not more than 5 per cent. excluding water.	Up to 200°; maximum, 2 per cent. Up to 250°; maximum, 25 per cent.	Up to 250°; maximum, 4 per cent.
Viscosity (Rütgers)	...	20 to 60 secs. at 50°.	...
Softening point	Not under 20° and not over 40°.	...	Not under 30° and not over 50°.

(*d*) Road Tar

(1) **Properties.**—The best road tars contain sufficient free-carbon to function as a filler; a limited amount of water-soluble constituents, phenols or bodies readily subject to polymerization and oxidation; sufficient high-boiling viscous oils, and such an amount of naphthalene as to effect a sensible reduction in the consistency of the tar and an increase in consistency as the naphthalene volatilizes, without impairing the soundness of the road surface. The amount of naphthalene is an indication of the proportion of its associated liquid hydrocarbons of a chemically stable nature.[2] The viscosity and distillate fractions must be adjusted within fairly narrow limits. To free the tar from certain proportions of light oils, naphthalene, phenols and most of the water

[1] D.I.N.-D.V.M. 2122; D.I.N.-D.V.M. 2136; D.I.N.-D.V.M. 2138, *Deutscher Normenausschuss*, Berlin, 1933; *cf.* Abraham, *Asphalts and Allied Substances*, London, 1937, p. 639.

[2] Butterfield, *J. Soc. Chem. Ind.*, 1928, 47, 293 T.

present, the usual procedure is to distil the tar up to a suitable temperature and then to blend the residue with the quantities of bitumen, oil, pitch or untreated tar to satisfy specification requirements. Continuous stills may be employed [1]; alternatively the consistency and composition of the tar may be adjusted at the point of recovery by centrifuging and partial oxidation.[2]

With vertical retort tars a high consistency is obtainable only by removal of a higher percentage of distillates than with horizontal retort tars, and since the readily evaporated oils are so removed, the resultant road tar dries at a slower rate. To obtain high consistency and a rapid rate of drying from vertical retort tar, a residue tar may be blended with a lightly-topped tar; occasionally a high-consistency tar may be prepared and setting be dependent on cooling instead of evaporation.[3] For a concise account of the properties and applications of road tars the work of Hughes, Adam and China [4] should be consulted. Details of Standard British, German and American Specification requirements are set out below :—

*British Standard Specifications for Road Tars.**

	Road tar I.	Road tar II.	Road tar III.
Specific gravity at 15° †	1·140 to 1·225	1·150 to 1·240	1·160 to 1·260
Maximum weight per cent. of water or ammoniacal liquor	0·5	0·5	0·5
Maximum weight per cent. of light oils (200°)	1·0	1·0	1·0
Distillate between 200° and 270°	9·5 to 21	8·0 to 16	6 to 12
Distillate between 270° and 300° (heavy oils)	3·5 ,, 12	3·5 ,, 12	3 ,, 8
Maximum volume per cent. of crude tar phenols	5·0	4·0	2·0
Maximum weight per cent. naphthalene	6·0	5·0	3·0
Free-carbon per cent. weight within the range	20	6·0 to 21	8 to 22
Consistency or viscosity (seconds), within the range	10 to 40 ‡ at 30·0°	40 to 125 ‡ at 25·0°	70 to 120 ‡ at 35·0°

* *British Standard Institution, B.S.* 76, 1930, and No. 76, Part 2, 1931.

† Tars produced from Scottish coals carbonized in vertical retorts are accepted if the minimum sp. gr. is not lower than 1·110 for Tar No. 1, 1·120 for Tar No. 2, and 1·130 for Tar No. 3, provided that such tars comply with the appropriate specification in all other details.

‡ Higher consistencies may be specified at the discretion of surveyors.

The above tars must be prepared in stills or dehydrating plant from coal tar produced in retorts or coke ovens, or in such other manner as approved by the engineer, except that the tars from which

[1] Sensicle, *Coke Oven Managers' Association*, Middlesborough, 25th April 1925.
[2] Sensicle, B.P. 257560, 1925.
[3] Chadder and Spiers, *Gas. J.*, 1930, **192**, 161.
[4] *Tar Roads*, London, 1938.

they are prepared must not contain more than 10 per cent. of carburetted water-gas tar. Tar No. 1 is specified for the surface-tarring of roads, Tar No. 2 for the manufacture of tar macadam for cold application, and Tar No. 3 for the manufacture of tar macadam laid by the hot or semi-hot process.

*German Standard Specifications for Road Tar-Bitumen Mixtures.**

	Types.			
	B.T. 40/70.	B.T. 80/125.	B.T. 140/240.	B.T. 250/500.
Appearance	Uniform	Uniform	Uniform	Uniform
Viscosity by Road Tar Consistometer (10 mm. orifice)—				
at 30°, seconds	40 to 70	80 to 125	approx. 140 to 240†	approx. 250 to 500†
at 40°, seconds	...	...	25 to 40	45 to 100
Melting-point (Ubbelohde, °C.)	...	...	approx. 25 to 29†	approx. 30 to 35†
Heating test. (See test regulations)	...	...	...	...
Distillation—				
Water, maximum weight per cent.	0·5		0·5	0·5
Light oils (up to 170°) maximum weight per cent.	1·0		1·0	1·0
Medium oils (170° to 270°) weight per cent.	7 to 15		1 to 11	1 to 7
Heavy oils (270° to 300°) weight per cent.	3 ,, 11		3 ,, 11	2 ,, 9
Maximum softening point, K and S, °C.	45		45	45
Phenols, maximum volume per cent.	2·5		2·5	2·0
Naphthalene, maximum weight per cent.	3·5		2·5	2·5
Specific gravity, maximum at 25°	1·17		1·19	1·21

* Specifications apply only to mixtures of 85 per cent. by weight Standard Road Tar with 15 per cent. by weight standard bitumen 45.

† Determination of viscosity is effected at 40°. Viscosity at 30° and the melting point are given for comparison.

*German Standard Specifications for Road Tars.**

<table>
<tr><th rowspan="2"></th><th rowspan="2">Cold road tars.</th><th colspan="6">Types.</th></tr>
<tr><th>T. 10/17.</th><th>T. 20/35.</th><th>T. 40/70.</th><th>T. 80/125.</th><th>T. 140/240.</th><th>T. 250/500.</th></tr>
<tr><td>Appearance</td><td>Uniform</td><td>Uniform</td><td>Uniform</td><td>Uniform</td><td>Uniform</td><td>Uniform</td><td>Uniform</td></tr>
<tr><td>Viscosity by Road Tar Consistometer:—</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>4 mm. orifice at 25°, maximum seconds</td><td>30</td><td>...</td><td>...</td><td>...</td><td>...</td><td>...</td><td>...</td></tr>
<tr><td>10 mm. orifice at 30°, seconds</td><td>...</td><td>10 to 17</td><td>20 to 35</td><td>40 to 70</td><td>80 to 125</td><td>approx. 140 to 240 †</td><td>approx. 250 to 500 †</td></tr>
<tr><td>10 mm. orifice at 40°, seconds</td><td>...</td><td>...</td><td>...</td><td>...</td><td>...</td><td>25 to 40</td><td>45 to 100</td></tr>
<tr><td>Melting-point (Ubbelohde, ° C.)</td><td>...</td><td>...</td><td>...</td><td>...</td><td>...</td><td>approx. 25 to 29 †</td><td>approx. 30 to 35 †</td></tr>
<tr><td>Test for bitumen mixture. (See test regulations)</td><td>...</td><td>...</td><td>...</td><td>...</td><td>...</td><td>...</td><td>...</td></tr>
<tr><td>Distillation:—</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>Water, maximum weight per cent.</td><td>0·5</td><td colspan="2">0·5</td><td colspan="2">0·5</td><td>0·5</td><td>0·5</td></tr>
<tr><td>Light oils (up to 170°), maximum weight per cent.</td><td>10 to 18</td><td colspan="2">1·0</td><td colspan="2">1·0</td><td>1·0</td><td>1·0</td></tr>
<tr><td>Medium oils (170° to 270°), maximum weight per cent.</td><td>10</td><td colspan="2">9 to 17</td><td colspan="2">2 to 12</td><td>1 to 8</td><td>1 to 6</td></tr>
<tr><td>Heavy oils (270° to 300°), maximum weight per cent.</td><td rowspan="2">16 to 32</td><td colspan="2">4 „ 12</td><td colspan="2">4 „ 12</td><td>3 „ 10</td><td>2 „ 8</td></tr>
<tr><td>Anthracene oil (300° to 350°), converted weight per cent.</td><td colspan="2">14 „ 27</td><td colspan="2">16 „ 30</td><td>17 „ 27</td><td>15 „ 25</td></tr>
<tr><td>Pitch residue, converted to 67°, softening point, K and S, weight per cent.</td><td>52 „ 62</td><td colspan="2">55 „ 65</td><td colspan="2">58 „ 68</td><td>61 „ 69</td><td>66 „ 74</td></tr>
<tr><td>Maximum softening point, K and S, of pitch, ° C.</td><td>70</td><td colspan="2">70</td><td colspan="2">70</td><td>70</td><td>70</td></tr>
<tr><td>Phenols, maximum volume per cent.</td><td>3</td><td colspan="2">3</td><td colspan="2">3</td><td>2</td><td>2</td></tr>
<tr><td>Naphthalene, maximum weight per cent.</td><td>3</td><td colspan="2">4</td><td colspan="2">3</td><td>3</td><td>2</td></tr>
<tr><td>Crude anthracene, maximum weight per cent.</td><td>3</td><td colspan="2">3</td><td colspan="2">3·5</td><td>3·5</td><td>4</td></tr>
<tr><td>Insoluble in benzole, weight per cent.</td><td>4 to 16</td><td colspan="2">5 to 14</td><td colspan="2">5 to 16</td><td>5 to 18</td><td>5 to 18</td></tr>
<tr><td>Adhesion test. (See test regulations)</td><td>...</td><td colspan="2">...</td><td colspan="2">...</td><td>...</td><td>...</td></tr>
<tr><td>Specific gravity, maximum at 25°</td><td>...</td><td colspan="2">1·22</td><td colspan="2">1·23</td><td>1·24</td><td>1·25</td></tr>
</table>

* D.I.N. 1995, *Deutscher Normenausschuss*, 1938.

† Viscosity determined in British Road Tar Consistometer at 40°. Viscosity at 30° and melting-point given for comparison.

American Standard Specifications for Road Tars.[1]

	D. 104-36 T.[2]	D. 105-36 T.[3]	D. 106-28 T.[4]	D. 107-28 T.[5]	D. 108-36 T.[6]	D. 109-36 T.[7]	D. 110-36 T.[8]	D. 111-36 T.[9]
Water, per cent. by weight	max. 2·00	max. 2·00	max. 2·00	max. 2·00	0·00	0·00	0·00	0·00
Softening point, Ring and Ball method.	...	...	...	...	...	...	30° to 40°	30° to 40°
Float test, seconds at 32°	...	...	...	...	60 to 150	60 to 150	...	...
Distillation (per cent. by weight on water-free material, total distillate) :—								
0° to 170°	max. 7·00	max. 5·00	1·00 to 8·00	1·00 to 8·00	max. 1·00	max. 1·00	max. 1·00	max. 1·00
0° ,, 235°	max. 20·00	max. 20·00	8·00 ,, 20·00	8·00 ,, 20·00	max. 10·00	max. 4·00	...	max. 2·00
0° ,, 270°	max. 30·00	max. 35·00	16·00 ,, 28·00	16·00 ,, 28·00	max. 15·00	max. 13·00	max. 10·00	max. 10·00
0° ,, 300°	max. 35·00	max. 45·00	max. 36·00	max. 36·00	max. 25·00	max. 26·00	max. 20·00	max. 20·00
Residue, per cent. by weight	min. 65·00	min. 55·00	min. 64·00	min. 64·00	min. 75·00	min. 74·00	min. 80·00	min. 80·00
Specific gravity at 25° of total distillate to 300°	min. 1·00	...	...	...	min. 1·02	...	min. 1·02	...
Softening point of residue from distillation, Ring and Ball method	max. 60°	max. 60°	max. 65°	max. 65°	max. 65°	max. 65°	max. 65°	max. 65°
Total bitumen soluble in carbon disulphide, per cent. by weight	88 to 97	min. 95	78 to 95	min. 95	78 to 95	min. 95	78 to 95	min. 95
Specific viscosity, 50 ml. at 40°	8 ,, 35	8 to 35	35 ,, 80	35 to 80	...	...	...	...

[1] Reverted to tentative status in 1936, except D. 106-28 T. and D. 107-28 T. These latter are tentative up to 1937.

[2] High carbon tar for surface treatment, cold application.

[3] Low carbon tar for surface treatment, cold application.

[4] High carbon tar cement for use cold in repair work (cut-back product).

[5] Low carbon tar cement for use cold in repair work (cut-back product).

[6] High carbon tar for surface treatment, hot application.

[7] Low carbon tar for surface treatment, hot application.

[8] High carbon tar cement for use in the construction of tar macadam and tar concrete pavements.

[9] Low carbon tar cement for use in the construction of tar macadam and tar concrete pavements.

The Float Test may be substituted for the Softening Point Test in Specification D. 110-36 T. and D. 111-36 T. above, the requirement then being a value of 100 to 200 secs. for the float test at 50°. With regard to the softening point, the range, within the above limits, should be 5° for any given locality, *i.e.* for cold climates 30° to 35° equivalent to a value for the float test at 50° of 100 to 160 secs. For warm climates, the values should be 35° to 40° for softening point, equivalent to 160 to 220 secs. for the float test at 50°. The sp. gr. determination at 25° is carried out by the Standard Method as for the determination of the sp. gr. at 38°. The specification range for total bitumen covers a wide variety of materials. A range of 88 to 95 per cent. should be specified for products from vertical retorts or low carbon coke-oven tars; for high carbon coke-oven or mixtures of coke-oven and gas-house tars a range of 78 to 88 per cent. should be specified. To meet the requirements of local conditions of temperature, road conditions and climate, materials should be specified, within the viscosity limits given above, under the ranges and headings, Light, 8 to 13; Medium, 13 to 18; Heavy, 18 to 25 and Extra Heavy, 25 to 35. The Specific Viscosity must be determined by the Standard Method,[1] and reported as specific viscosity compared with water at 25°.

In Germany more viscous tars of a special nature are manufactured for repeated road surfacing and the manufacture of tar concrete. Weather tar, a patented product of the Verkaufsvereinigung für Teererzeugnisse G.m.b.H., Essen, has the following properties[2]:—

Sp. gr. at 25° not more than	1·24
Per cent. water not more than	0·5
Drip-point, above	30°
Solidification point, below	−25°
Volatility:—	
Not more than 1 per cent. distillate up to	270°
,, ,, 5 ,, ,, ,,	300°
Acid oils	...
Naphthalene	none
Free-carbon, not more than	18 per cent.

Many road tars are improved by the addition of a proportion of asphaltic bitumen,[3] but some may be so deteriorated if the bitumen

[1] Bull. No. 1216, U.S. Dept. of Agriculture.

[2] Mallison, *Proc. Third International Conference on Bituminous Coal*, 1931, vol. i., p. 947.

[3] Temme, *Bitumen*, 1932, **2**, 139, 143; Spiers, *J. Soc. Chem. Ind.*, 1926, **45**, 396 T; Mallison and Soltau, *Brennstoff-Chem.*, 1927, **8**, 169; Ehlgötz and Flister, *Teer u. Bitumen*, 1933, **31**, 405, 417, 429; Evans and Pickard, An Investigation into the Nature and Properties of Coal Tar, South Metropolitan Gas Co., 1931, 28, 29; Adam and co-workers, *J. Soc. Chem. Ind.*, 1937, **56**, 417 T.

is not truly asphaltic in character. Generally speaking, such mixtures as surface dressings hold a larger quantity of grit or chippings. In Germany it is customary to limit the proportion of asphaltic bitumen to 15 per cent.; by the addition of this material the tar is made more viscous.

(2) **Cold Tar.**—Cold tar is prepared by the addition of volatile solvents to a road tar, so that it is fluid at ordinary temperatures and may be applied by spraying; its fluidity gives pronounced penetrability. Cold tars are so prepared from standard road tars and such solvents as light oils, heavy benzole and alcohol. In America they are widely used.

According to Mallison,[1] in the preparation of a cold tar due consideration must be given to its use. If the tar is to be used for repair work or the making of tar macadam, it must contain a high proportion of a strong binding material, such as a suitable pitch; if for the restoration of old surfaces a certain content of tar oil will be required to soften and make pliant the hardened existing surface. The manner of application, by sprays or otherwise, and seasonal temperature variations must also be kept in mind. Cold tars having flash-points higher than about 30° can be considered to be practically free from danger.

(a) *Flash-point.* If a Pensky-Martens apparatus is not available, the cold tar may be tested by filling a 250 ml. bottle about half-way with the tar, well corking the bottle and allowing to stand for about two hours. The cork is then drawn with the left hand, and with the right hand a lighted match is dipped into the air-filled space above the cold tar. The occurrence of a flash, or otherwise, is noted. As additional tests to determine the suitability of a sample of cold tar for specific application the following are proposed by the Deutscher Strassenbauverband:—

(b) *Loss by Vaporization.* 50 g. of the sample of cold tar is weighed into a tared brass bowl which measures 12·8 cm. interior diameter (surface area, 128 sq. cm.) and 1·5 cm. interior depth, the cold tar being distributed as evenly as possible. The bowl is allowed to stand, free from draught and dust, at a uniform room temperature of approximately 20° in a shaded position for three days and then reweighed. The loss in weight is expressed as percentage loss. In like manner the percentage loss after ten days and after thirty days is ascertained. The percentage loss, after five hours and after ten hours, at 50° is also determined by heating 50 g. of the sample in a brass bowl in an oven maintained at $50° \pm 1°$. The bowl must be cooled in a desiccator.

(c) *Binding Test.* 5 g. of the sample of cold tar is mixed with

[1] *International Road Tar Conference*, Lucerne, 14th June 1933; *Gas. J.*, 1933, **202**, 862.

100 g. of dry basalt gravel (size 3 to 7 mm., and free from dust) in a brass bowl of the above dimensions, using a broad wooden spatula. The depth of the layer of the mixture is approximately 1 cm. After standing for twenty-four hours the mixture should be cohesive, *i.e.* no covered particles of gravel should fall out when the bowl is held in a perpendicular position for a period of at least fifteen seconds.

Hot application of standard road tars is common practice in Germany. For cold application emulsions of the tar-in-water type are also used for surface tarring, for inner impregnation, for patching, and for application when the surface is not dry. Great variation in effectiveness is found, some emulsions remaining stable for long periods ; in the case of others the emulsion breaks early and gives rise to faulty work and considerable waste. Generally these oil/water emulsions contain about 50 per cent. of water (range 30 to 80 per cent.) and about 1 per cent. of emulsifying agent. The softening point of the bitumen used is about 40°, although material of softening point up to 60° may occasionally be used. Clayton [1] discusses tests of a specialized character connected with these emulsions. In Germany the manufacture of tar emulsions has made great progress, and accordingly specifications and tests are included in the German Standards, D.I.N. 1995 and D.I.N. 1996. The following data are abstracted therefrom :—

(*e*) Tar Emulsions

1. **German Requirements.**—The emulsion must be uniform ; if tar separates it must be emulsified on shaking strongly, and the emulsion must remain uniform at least seventy-two hours. The content of tar must not be less than 48 per cent. by weight, and the tar must conform to the requirements for German road tars (p. 381). When a layer of the emulsion is placed on a porcelain or dense stone surface (as, for example, a freshly fractured surface of granite), a film or skin must form within one hour. After twenty-four hours drying at room temperature in a current of air, the film should adhere so tenaciously to the porcelain or stone surface that it will neither peel off nor be readily removed.

When placed in distilled water, the film must not dissolve nor become distorted, and holes must not form within the film. The water must not become brown in colour, nor must the tar re-emulsify. If the emulsion is used in admixture with asphalt or tar for cold applications, it must remain as an emulsion during the mixing, and separation must not take place. Emulsions must be stable on storage in closed vessels, any light separation which has taken place over a period of six weeks or owing to the effect of frost, being readily removed

[1] Clayton, *Chem. and Ind.*, 1932, 51, 129.

by stirring. If the emulsion is to be used in structures, it should be applied in dry weather, and upon a foundation which allows for the percolation of water.

2. **German Tests.**—Tar emulsions are tested for sp. gr., particle size, dilution in water, stability on storage and to frost, behaviour towards acid, filming properties, behaviour on application to dry and moist sand, and for the content of tar (and/or asphalt). Other tests which may be applied are those commonly used for the testing of road tars.

(a) The *colour*, *odour* and *uniformity* of the emulsion are observed. If the emulsion has separated, a test should be applied for re-emulsification by simple shaking.

(b) *Specific Gravity* is determined by a hydrometer at 15°.

(c) *Particle Size* is determined by microscopic examination.

(d) *Dilution with Water.* 100 ml. is diluted with increasing quantities of (*a*) distilled water and (*b*) tap water. An observation is made, if and when flocculation begins.

(e) *Stability.* 150 ml. of the emulsion is poured into a measuring cylinder, 30 cm. in height and 3·5 cm. in diameter, and allowed to stand for eight days. Separation of water or tar is noted. The material is then well shaken, and an observation is made to determine whether the original uniformity of the emulsion is obtained. To determine the stability of the emulsion to frost, 50 ml. of the emulsion is placed in a glass cylinder of 2·5 cm. diameter, cooled for three hours at −8° in a salt solution, and then allowed slowly to attain room temperature. The emulsion, after shaking, must be completely uniform and must exhibit no signs of flocculation. The latter test must be repeated five times.

(f) *Behaviour towards Acid.* 100 g. of the emulsion is mixed with 250 ml. of distilled water and small quantities of normal hydrochloric acid added, until the whole of the tar separates out. The quantity of acid required is noted, as well as the nature of the separation, *i.e.* as to whether the masses adhere, or are precipitated as a loose sludge.

(g) *Filming Properties.* A small quantity of emulsion is distributed on the inner surface of a porcelain dish, any excess of emulsion being run off. The dish is placed on a level surface and maintained at room temperature, and the time required for a continuous film to form is observed. In the case of a stone surface, the stone is suspended by a thread, dipped into the emulsion, and the same procedure is adopted. The effect of distilled water and tap water is noted, the film being rinsed to ascertain whether it can be removed, and if so, its manner of breaking.

The adherent capacity of the film rapidly increases with progressive

drying, and after twenty-four hours it should not be possible to lift the film from the basin with the finger; similarly with films formed on stone surfaces.

(h) *Behaviour on Application to Dry and Moist Sand.* This test is carried out, first with dry sand, and then with moist sand of 4 per cent. water content. The sand is placed in a glass dish 4 to 5 cm. in height, levelled, and the emulsion poured on to it on one side of the dish. The emulsion is then distributed by tilting the dish, excess is removed, and the operation carried out so that the layer is uniform. Observations are made as to whether the emulsion is absorbed by the sand, or remains on the upper surface. The time of filming of the emulsion is noted. Further quantities of emulsion are mixed with dry and wet sand, the sand being then spread out as a thin layer and allowed to dry in the air. This part of the test is to ascertain, principally, whether the mixture of emulsion and sand takes place without the breaking of the emulsion and whether the emulsion has any cementing action on the sand grains.

(i) *Water Content* is determined by distillation of 8 g. of the emulsion and 50 ml. of xylole.

(j) *Tar Content.* In the case of asphalt emulsions, water is removed by evaporation on the water bath. The water-free asphalt is treated with benzole, filtered, and the benzole extract then washed with alcohol (50 per cent.) and distilled water to remove the emulsifying agent and other constituents. The asphalt is now recovered by evaporation of the benzole solution.

In the case of certain tar emulsions a similar method may be adopted; alternatively the tar may be recovered by distillation, during the water determination, or the tar content may be estimated by the combination of these two methods. Other methods may be applied with advantage, as for example, centrifuging.

3. **British Requirements.**—The British Standard Specification for road tar emulsions and road tar-asphaltic bitumen mixtures [1] applies the following definitions :—

(a) *Road Tar.* Tar prepared in stills or dehydrating plant from tar produced as a by-product of the carbonization of coal in retorts, or in coke-ovens, or in such manner as may be expressly approved in writing by the Engineer, except that the tar from which it is prepared may contain not more than 10 per cent. of the tar produced in the manufacture of carburetted water gas.

(b) *Asphaltic Bitumen.* Natural or naturally occurring bitumen or bitumen prepared from natural hydrocarbons, or from derivatives of natural hydrocarbons by distillation or oxidation or cracking; solid or viscous, containing a low proportion of volatile constituents,

[1] Extracted by permission from *B.S.* 618, 1935.

possessing characteristic agglomerating properties, and substantially soluble in carbon disulphide.

(c) *Road Tar or Road Tar-Asphaltic Bitumen Emulsion.* A liquid product in which a substantial amount of road tar or of road tar-asphaltic bitumen mixture is suspended in a finely divided condition in an aqueous medium by means of one or more suitable emulsifying agents.

The following requirements are specified :—

1. *Composition.* The emulsion shall contain only water, emulsifying agents and road tar, or road tar-asphaltic bitumen mixture. No other materials shall be present.

2. *Road tar.* The road tar used for the manufacture of the emulsion shall conform to the requirements of *B.S.* 76, 1930, Tar (No. 2) for Road Purposes, or *B.S.* 76, Part 2, Tar (No. 3) for Road Purposes, except that tars otherwise conforming to this latter specification, but of higher viscosity, may be employed.

3. *Road tar-asphaltic bitumen mixtures.* Road tar used for the manufacture of the emulsion shall conform to (2) above and the asphaltic bitumen to the following:—

The penetration at 77° F. (25° C.) shall not be less than 25 nor more than 350. The solubility in carbon disulphide shall not be less than 99 per cent.

The content of asphaltic bitumen in the mixture shall not exceed 20 per cent. The mixture shall be of such a consistency that its penetration at 77° F. (25° C.) is not less than 55, and its viscosity (determined at 30° C. by the B.R.T.A. viscometer) is not lower than forty seconds.

4. *Emulsifying agent.* The emulsifying agent shall be such that any drainings, washings, or the like, passing from the work into streams, ponds, rivers, etc., shall not, after dilution in the said waters, have any deleterious effect upon plant or fish life. The emulsifying agent shall not be present in such concentration in the emulsion that it exerts any deleterious effect on the road tar or road tar-asphaltic bitumen mixture deposited. The amount shall not normally exceed 2 per cent. by weight of the emulsion; if this amount is exceeded the amount shall be certified by the manufacturer. The percentage of the emulsifying agent shall be reckoned in its dry state.

5. *Water content.* The emulsion shall not contain more than 40 per cent. by weight of water.

6. *Residue on sieving.* The emulsion shall not show more deposit than 0·25 g. per 100 ml. of emulsion.

7. *Coagulation of binder.* The emulsion shall not exhibit coagulation of binder exceeding 0·1 g. per 100 ml. of emulsion.

8. *Coagulation of emulsion at low temperatures.* The emulsion shall show no coagulation when tested in the manner specified.

9. *Stability in bulk.* The emulsion shall not show greater loss of binder than is represented by a maximum difference in initial and final average water content of 3 per cent. when tested in the manner specified.

10. *Viscosity of emulsion.* The emulsion, where the road tar or road tar-asphaltic bitumen content is not greater than 65 per cent., shall have a viscosity at 20° C. between 5 and 20 degrees when tested in the Engler viscometer in the manner specified.[1] For emulsions with a content of road tar or road tar-asphaltic bitumen exceeding 65 per cent., no high limit is specified.

11. *Sedimentation.* The emulsion shall not show more sedimentation than is

[1] *British Standards Institution, B.S.* 434, 1935.

indicated by a maximum difference of 5 per cent. between the water content of the original emulsion, and that of either the top or bottom portions, when tested in the manner specified.

4. **British Tests.**—Sampling of the tar shall be carried out in accordance with the appropriate methods given in *Standard Methods for Testing Tar and its Products* [1]; the sampling and testing of the asphaltic bitumen in accordance with the appropriate methods given in *Standard Methods of Testing Petroleum and its Products* (3rd edn., 1935), and the sampling of the emulsion in accordance with the methods given in *B.S.* 618, 1935. The special tests are carried out as follows :—

(a) *Water Content.* About 30 to 40 g. of the emulsion is weighed into a standard 500 ml. distillation flask, which is provided with a standard condenser.[2] An equal volume of diluent is then added. The diluent must conform to the following requirements :—

Sp. gr., 15·5°/15·5°, not lower than 0·8545 ; free from water and visible impurities at 15·5° ; distillation of 100 ml. by standard method to give, up to 125° (running point), not more than 5 ml. ; 91 ml. of distillate up to 160° (stop-point) ; and on steam distillation of residue until 50 ml. of water condensed, no greasy or oily residue shall then be visible. British Standard Pure Xylole, 3° Xylole, 5° Xylole, and Coal Tar Solvent Naphtha conform to these requirements.[3] Before use the diluent shall be allowed to stand in contact with water until saturated.

0·5 g. of powdered anhydrous potassium bisulphate and one or two glass beads are added to the distillation flask and the apparatus assembled. Distillation is continued, into a special tube of 25 ml. capacity (graduated in 0·1 ml. and accurate to 0·05 ml.), until no more water distils over as shown by the clarification of the distillate. The apparatus is allowed to cool, and exactly 5 ml. of 10 per cent. aqueous sodium hydroxide solution introduced into the graduated receiver by way of the condenser. This produces a clear, easily readable meniscus. The volume of water is noted, after making allowance for the sodium hydroxide solution added.

(b) *Residue on Sieving.* 100 ml. of the emulsion is passed through a clean circular sieve of 1·5 in. (38 mm.) diameter, of British Standard Mesh No. 30, and previously weighed and moistened, first with industrial alcohol which is later removed by means of distilled water. The emulsion is poured rapidly upon the wetted sieve and a constant layer of emulsion maintained upon the sieve and gently agitated with a glass rod, which latter must not be allowed to touch

[1] p. 121. [2] *Institute of Petroleum*, *Serial* F. O. 14.

[3] *British Standards Institution*, *B.S.* 458, 1939 (price 3s. 6d.); and *B.S.* 479, 1939 (price 3s. 6d.).

the sieve itself. When the emulsion has passed through, the sieve is washed with distilled water until all the emulsion has been removed. The amount of the deposit is determined by drying the sieve and contents in a vacuum desiccator for twenty-four hours and weighing.

(c) *Coagulation of Binder.* The emulsion is sieved in the manner described above (b). 100 ml. of the sieved sample is transferred to a glass measuring cylinder approximately 27 mm. internal diameter and 180 mm. in height (to surface of liquid), the cylinder closed with a rubber stopper and allowed to stand for seven days in a position not subject to wide temperature variations. Thereafter the emulsion is well stirred by means of a glass rod and sieved in the manner described above (b). The cylinder must be drained as completely as possible, and afterwards washed with distilled water until free from emulsion and other residue, the washings being passed through the sieve.

(d) *Coagulation at Low Temperatures.* The apparatus used consists of a glass boiling tube 6 in. (150 mm.) long and 1 in. (25 mm.) internal diameter, provided with a cork, through a hole in which passes loosely a thermometer graduated down to $-10°$, the ungraduated stem extending beyond the cork. Into the boiling tube is introduced 20 ml. of the emulsion. The emulsion is heated by placing the tube in water maintained at 50° and stirring gently with the thermometer until the temperature of the emulsion is constant. The tube is now placed in a 600 ml. beaker containing ice-water, at the bottom of which is a mass of finely crushed ice, retained by a piece of wire gauze fitted into the beaker. As soon as the temperature of the emulsion no longer falls, salt is added to the ice-water until the temperature of the freezing mixture reaches $-1°$ to $-1{\cdot}5°$, thus reducing the temperature of the emulsion, which is still being slowly stirred, to 0°. When the emulsion reaches this temperature, stirring is discontinued. The tube is then transferred to a second 600 ml. beaker of freezing mixture at a temperature of $-3°$ to $-4°$ and the emulsion allowed to remain quiescent in this mixture for thirty minutes. The thermometer must not be allowed to touch the sides of the tube when carrying out this part of the test. The tube is then removed without disturbance and the temperature of the emulsion allowed to rise spontaneously to room temperature. The emulsion is then passed through a sieve of British Standard Mesh No. 22, and the tube washed free from emulsion and other residue with distilled water and the washings passed through the sieve, when the coagulated tar or asphaltic bitumen, if any, will be retained.

(e) *Stability in Bulk.* This test must be made on the contents of a selected container of from 30 to 40 gals. capacity. From the emulsion

as received an average sample must be taken by the specified method, and the water content determined (*vide supra*). The bulk of the emulsion is then emptied into a suitable clean cylindrical container which must be sealed air-tight and allowed to stand on end for three months in a location not subject to large temperature variations. At the end of this period an average sample of the contents is taken by the specified method, and passed through a sieve of British Standard Mesh No. 22. The water content of the sieved emulsion is then

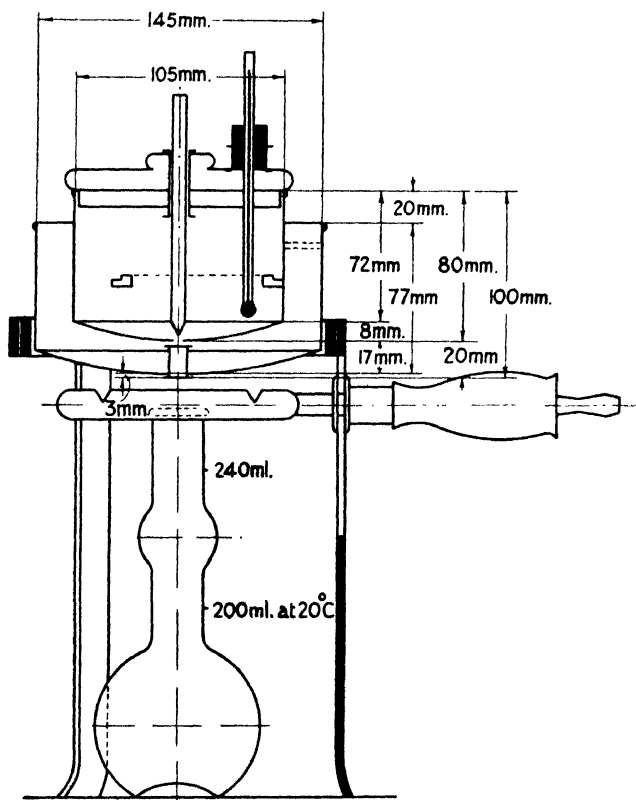



FIG. 53.

determined by the specified method and the difference between this and the initial average water content is evaluated.

(f) *Viscosity.* The apparatus used consists of a standard Engler viscometer, fitted with a stirring device in the outer bath, and carrying a thermometer (10° to 50°) in both the inner and outer baths. The receiving flask has a capacity of 200 ml. at 20° (Fig. 53).

The water value is first determined as the time in seconds of efflux of 200 ml. of distilled water at 20°, care being taken to follow precisely

the instructions given for the cleaning of the inner vessel, the setting of the viscometer in a horizontal plane, the use of the appropriate stopper, and the filling of the inner vessel with water and its discharge. Series of repeat determinations must be made until constant times of efflux are found. The mean of the six values of the last two series is taken as the time of efflux of water, and the value must lie between the limits of forty-seven and fifty-three seconds. The first series of experiments is regarded as finished when three results have been obtained differing by not more than 0·5 seconds, and the values show no progressive decrease.

The emulsion to be tested is passed through a sieve of British Standard Mesh No. 30, and warmed in a bath at a temperature slightly in excess of 20° until it is at a uniform temperature.

The water in the jacket of the viscometer is brought to 20°, the emulsion poured into the instrument, carefully brought to the correct height and the viscometer levelled. When the inner and outer temperatures are steady at 20° the time of efflux of 200 ml. of emulsion is determined, the emulsion being allowed to fall down the side of the receiving flask to eliminate frothing. The time of efflux for 200 ml. of the emulsion divided by the time of efflux for 200 ml. of water gives the viscosity in Engler degrees. Three determinations must be made on each sample and the mean value taken. If the extremes of the three determinations differ by more than 5 per cent. of the mean value a fresh test must be made on new material. The container must be washed out with distilled water after each determination, and dried with filter paper. The jet must also be thoroughly cleaned, using a spill of soft filter paper moistened with xylene. Irregular readings may result owing to moisture deposited on the bottom of the jet due to heating the instrument with gas. If difficulty is encountered through blockage of the jet of the viscometer, the emulsion must be further strained through a British Standard Mesh No. 60.

(g) *Sedimentation.* The water content of the emulsion is first determined (p. 389). A flat-bottomed glass cylinder is used of 1·5 in. (3·8 cm.) internal diameter, and 6 in. (15·2 cm.) in height, having side arms which are 1 in. (2·54 cm.) long and 0·125 in. (3·2 mm.) internal diameter, sealed in at heights 1·75 in. (4·44 cm.) and 3·5 in. (8·88 cm.) from the bottom. To each side arm is attached a short piece of rubber tubing which is closed with a spring clip, placed as close as possible to the end of the glass tube. The cylinder is graduated to 150 ml. 150 ml. of the emulsion is placed in the cylinder, the top of the cylinder closed with a cork or rubber stopper, and the cylinder then allowed to stand for seven days in the dark in a position not subject to wide temperature variations.

Thereafter the top portion of approximately 50 ml. is run off by

cautiously opening the clip on the top side arm. The middle portion is similarly run off into another container, using the lower side arm. Draining is considered complete when no further drop falls for a period of thirty seconds. Finally the bottom portion is emptied into a third container after gently shaking the cylinder to homogenize the contents. The water contents of the top and bottom portions are determined (p. 389) and the respective differences from the initial average water content are evaluated.

(f) Testing of Road Tars

Prescribed tests for road tars adopted by the British Standards Institution are those described in the 1929 edition of *Standard Methods*. Tars are tested for sp. gr., viscosity, tar acids, naphthalene, free-carbon and range of distillation and water content. Before testing, the sample must be thoroughly mixed by vigorous agitation in a sufficiently large vessel. For this purpose, to render the tar fluid, the container may be heated at a temperature not exceeding 60°, preferably in a water-bath, but a naked flame or other source of intense heat must not be used.

The British Standard specifications for road tar have been and will for some time be the subject of close study among the experts in the manufacture and use of these materials and many specifications are likely to be revised. A number of investigators are attempting to correlate field experience with practical laboratory testing and any revised specifications will reflect the result of their work. For the moment the developments are related to attempts to formulate an extended scale which will cope with viscosities from those of the thinnest commercial tars to the thick tars which border on soft pitches. This development is considered under the sub-section on viscosity (2) below. The Standard Methods for the several tests for road tars are dealt with in their normal sequence as follows on the basis of the current edition of *Standard Methods*, which anticipates revision of the road tar specifications :—

1. *Specific Gravity*. The sp. gr. is determined in routine practice by means of a hydrometer, but for reference tests the bottle should be used. Many tars are too thick to allow the stopper of the bottle to be pressed into position if the bottle is filled with tar. The bottle is then only partly filled, but to at least 50 per cent. of its capacity, and is maintained between 50° and 60° C. for half an hour in order that entangled air bubbles may escape. After cooling and weighing, the bottle is filled up with water at the specified temperature, the filled bottle being weighed. The water content of the bottle at the specified temperature is also ascertained.

If the determination is made at 15·5° C. and

W_1 = weight in g. of water required to fill the bottle completely at 15·5° C.,
W_2 = weight in g. of tar placed in the bottle and
W_3 = weight in g. of water required to complete the filling of the bottle at 15·5° C. after the tar has been weighed into the bottle, then

$$S_{15\cdot5^\circ C./15\cdot5^\circ C.} = \frac{W_2}{W_1 - W_3} + A'$$

where A′ is a correction for the buoyancy effect of the air, the value of $W_2/(W_1 - W_3)$ giving the appropriate value of $S'_{15\cdot5^\circ C./15\cdot5^\circ C.}$ for obtaining the required correction from buoyancy tables.

If the determination be made at some temperature t° C. other than 15·5° C. and

${}_tW_1$ = weight in g. of water required to fill the bottle completely at t° C.;
W_2 = weight in g. of tar placed in the bottle; and
${}_tW_3$ = weight in g. of water required to complete the filling of the bottle at t° C. after the tar has been weighed in the bottle, then

$$S_{t/t} = \frac{W_2}{{}_tW_1 - {}_tW_3} + A'$$

where A′ is the correction obtained from buoyancy tables, as before.

The sp. gr. $S_{15\cdot5^\circ C./15\cdot5^\circ C.}$ is

$$\frac{1}{{}_w\rho_{15\cdot5}}\left[S_{t/t} \times {}_w\rho_t + \beta(t - 15\cdot5)\right]$$

where

${}_w\rho_{15\cdot5}$ = density of water in g./ml. at 15·5° C.;
${}_w\rho_t$ = density of water in g./ml. at t° C.; and
β = change in density of the tar in g./ml. per °C. change in temperature (see p. 130).

2. *Viscosity.* Viscosity or consistency is a most important factor in the use of road tar. Limits of viscosity were first specified by the Ministry of Transport in 1923 in terms of readings on the Hutchinson viscosity gauge or tar spindle.[1] The standard viscometer developed by the Standardization of Tar Products Tests Committee in co-operation with the British Road Tar Association is now exclusively prescribed for use in determining conformity with British specifications, notably those of the British Standards Institution.[2] The British standard instrument was very quickly adopted on the Continent, notably in

[1] B.P. 22042, 1911. [2] *B.S.* 76, 1930, and *B.S.* 76, part 2, 1931.

Germany, after its first appearance. In the 1938 revision of *Standard Methods*, the experience of British workers was pooled with that of members of the International Tar Conference, and the provisions of *Standard Methods* 1938 have been accepted by all the countries

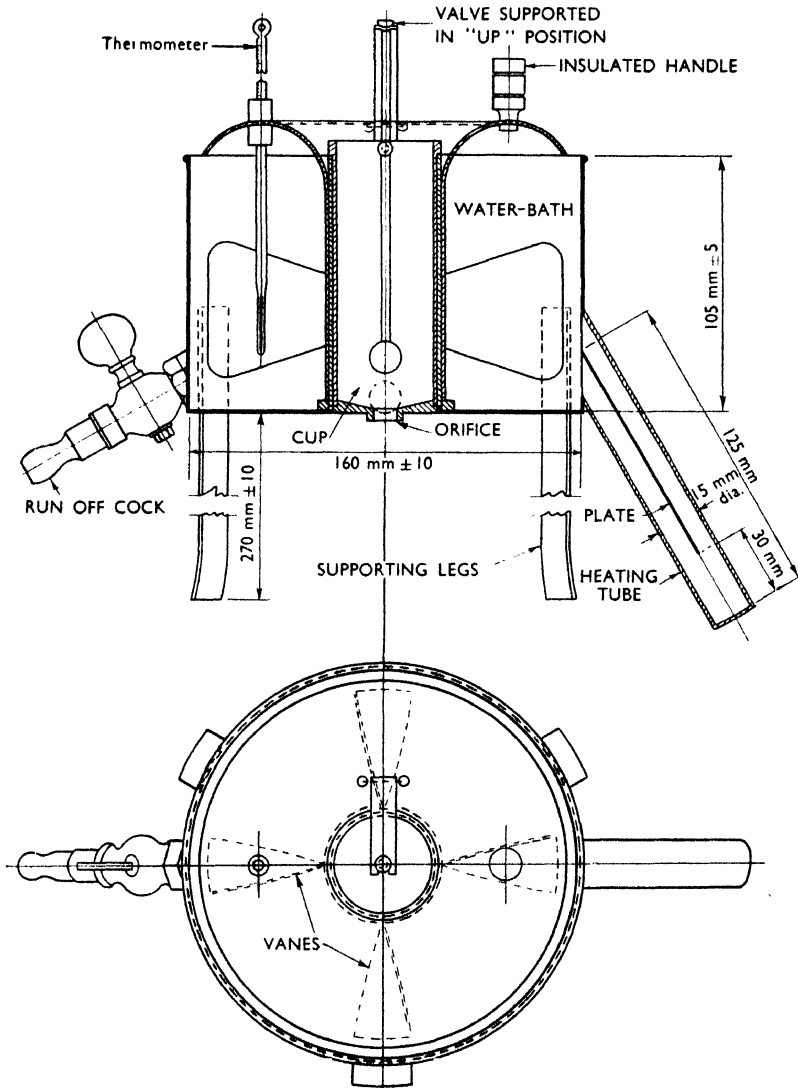



FIG. 54.—Viscosity of Refined Tar—Elevation and Plan of Assembled Viscometer.

adhering to the Conference. Since this formal adherence was recorded, however, it has been found that the Continental practice of using total immersion thermometers without corrections for emergent stem is continuing in connection with this test; it is liable to cause significant differences in the testing of certain tars when such thermometers are

used to replace that specified in the agreed British method. Investigations are still proceeding.

The instrument is a modification of the Redwood viscometer. It is shown assembled in Fig. 54, while Figs. 55 and 56 show supplementary details. Where many samples are to be tested, a large bath, provided with a mechanical stirrer and thermostatic control, and several cylindrical sleeves to carry the tar cups, will be found advantageous.

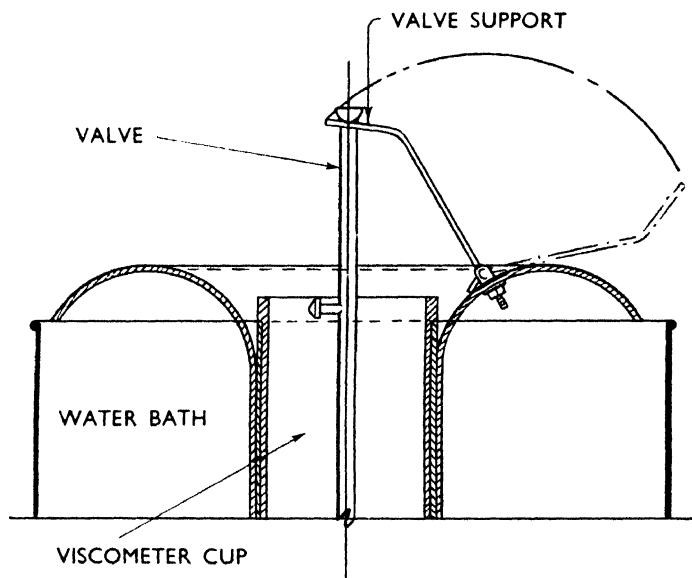



FIG. 55.—Viscosity of Refined Tar—Section showing Arrangement of Valve Support.

In the method internationally agreed, details are the result of studies aimed at either facilitating the procedure or eliminating obscure causes of lack of agreement between the results of independent tests—an aspect of considerable significance in the marketing of refined tars where consumption follows very quickly on delivery. The original text of the Standard Method must therefore be consulted and it will be sufficient here to say that 30° C. is the recognized standard test temperature, and that there are alternative standard temperatures (*e.g.* in the testing of No. 3 tar) of 35°, 40° C., etc. It is essential that the temperature of test be included as part of the report.

When carried out in strict accordance with the Standard Method the results should fall within ± 4 per cent. of the average of the several readings, a degree of accuracy considered satisfactory, having regard to the temperature-susceptibility of the viscosity of tars.

As will be seen from Fig. 56, the primary standard tar cup has

an orifice 10 mm. in diameter. In such an instrument, however, the testing of certain tars would give a viscosity reading so low that accurate measurement of the time of flow would be difficult, while with certain other tars so long a time of flow would be involved as to interfere with true stream-line flow through the orifice. Within a limited range these influences can be eliminated by choosing an appropriate temperature of test, so that the efflux time lies within the range 10 to 140 seconds. In order that the test may be applied to the full range of tars for which viscosities are at present required,

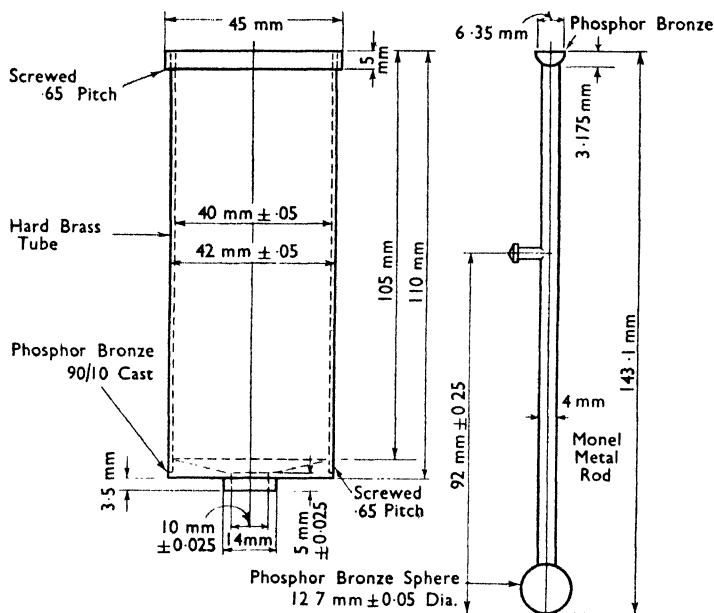



FIG. 56.—Viscosity of Refined Tar—Standard 10 mm. Tar Cup and Valve therefor.

an alternative standard tar cup has been adopted, the orifice in this case having a diameter of 4 mm. An alternative valve is used for this cup.

Spiers [1] has investigated the mathematical relationship between consistency (or viscosity) as determined by the Hutchinson tar gauge, and temperature. In this connection the work of Mallison and Soltau [2] should also be consulted.

Evans and Pickard [3] have carried out important investigations on the consistency and viscosity of coal tars and pitches. The relationship between consistency and temperature of tars and similar bituminous

[1] *J. Soc. Chem. Ind.*, 1926, 45, 396 T; *ibid.*, 1927, 46, 329 T.
[2] *Brennstoff-Chem.*, 1927, 8, 169.
[3] *An Investigation into the Nature and Properties of Coal Tar*, South Metropolitan Gas Company, London, 1931.

materials may be expressed by the formula, $CT^n = a$, where C represents the consistency as usually determined, *e.g.* in seconds of flow with efflux viscometers, T the temperature in degree Fahrenheit, and n and a are constants.[1] The above expression, expressed logarithmically, becomes log. C+n log. T = log. a, which is the equation to a straight line. Thus, determinations of consistency at two different temperatures suffice to establish, over a limited temperature range, the consistency-temperature relationship of a bituminous material. The effect of the addition of varying amounts of certain chemical compounds upon the consistency of a synthetic road tar is shown in the following table :—

Compound.	Addition per cent.	T_1° F.	T_2° F.	Consistency at T_1, seconds.	Consistency at T_2, seconds.	Calculated constants.		Consistency at 25°, Redwood No. 2, seconds (calculated).
						n.	a.	
Benzene .	2·5	68	95	1060·0	171·0	5·5	129×10^{11}	543
	5·0	68	95	381·5	103·0	3·9	532×10^{7}	234
	10·0	68	95	111·5	40·0	3·1	541×10^{5}	77
Phenol .	2·5	95	122	306·5	76·5	5·6	369×10^{11}	1010
	5·0	95	122	191·5	45·5	5·7	355×10^{11}	627
	7·5	95	122	140·5	38·0	5·2	269×10^{10}	416
	10·0	95	122	110·0	33·5	5·7	214×10^{9}	292
Aniline .	2·5	104	122	128·0	55·5	5·2	394×10^{10}	610
	5·0	104	122	76·5	37·5	4·5	911×10^{8}	295
	7·5	104	122	60·0	27·5	4·9	459×10^{9}	261
	10·0	104	122	37·0	20·0	3·8	171×10^{7}	116
β-naphthyl-amine	2·5	122	149	72·5	26·0	5·1	315×10^{10}	754
	5·0	122	149	57·0	23·0	4·5	138×10^{9}	448
	7·5	122	149	50·5	20·5	4·5	124×10^{9}	400
Naphthalene	2·5	95	122	254·0	68·0	5·3	777×10^{10}	780
	5·0	95	122	173·0	48·7	5·1	213×10^{10}	509
	10·0	95	122	74·5	24·0	4·5	588×10^{8}	190
	15·0	95	122	43·0	15·2	4·1	546×10^{7}	100
	20·0	95	122	24·5	11·5	3·0	209×10^{5}	45·8
β-naphthol .	2·5	113	122	136·5	88·0	5·7	688×10^{11}	1214
	5·0	113	122	115·5	72·0	6·1	386×10^{12}	1200
	7·5	113	122	106·5	66·5	6·1	356×10^{12}	1109
Synthetic tar	...	122	149	91·4	29·2	5·7	712×10^{11}	1260

The logarithmic temperature-consistency relationships for all the tars examined are included in Fig. 57.

It is to be remarked that the addition of neutral or basic hydrocarbons causes a much greater reduction in viscosity than corresponding quantities of phenolic compounds. The successive addition of aromatic compounds, such as naphthalene, etc., anthracene oil or pitch to a tar

[1] *Cf.* Herschel, *Ind. Eng. Chem.*, 1922, **14**, 715 ; Slotte, *Beiblätter*, 1892, **16**, 182.

causes a regular radial change in the position and slope of the logarithmic temperature-consistency curves of the mixtures, these radial curves emanating from a common focus. The free-carbon of a tar insoluble in pyridine has a negligible effect on the consistency of a pitch, whereas the free-carbon soluble in pyridine, but insoluble in benzene, exerts a very pronounced effect (p. 407). Using a " Metro Plastimeter " to measure the consistency of pitch at atmospheric

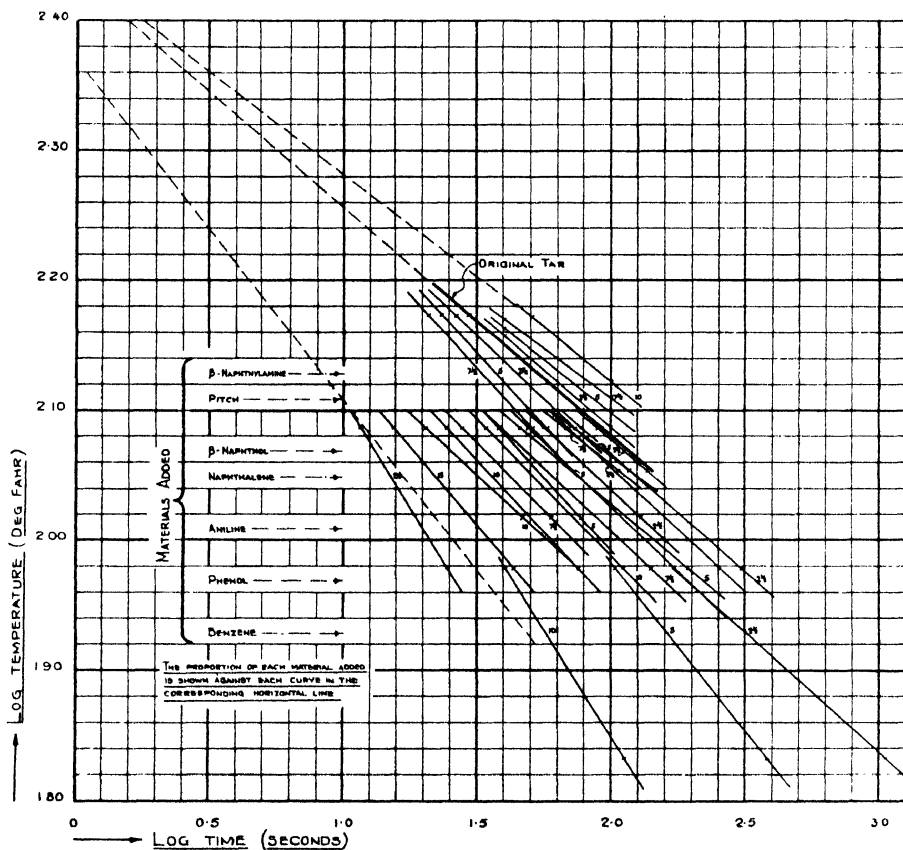



Fig. 57.

temperatures these authors conclude that, within practical limits of accuracy, pitch behaves as a true fluid at these temperatures in that it exhibits no anomalous consistency effects in its velocity-load relationship. Asphaltic bitumen, on the other hand, exhibits anomalous consistency effects in its velocity-load relationship.

Mitchell and Lee[1] have investigated the relationship between viscosity and temperature and show that for road tars and pitches the relationship conforms to $\eta T^n = a$, where η is viscosity, T

[1] *J. Soc. Chem. Ind.*, 1935, **54**, 407 T; 1936, **55**, 167 T.

is temperature °F. and n and a are constants. n has been termed the logarithmic temperature coefficient and is defined as $(\log . \eta_1 - \log . \eta_2)(\log . T2 - \log . T1)$; for tars of various viscosity obtained from the same source $\eta \propto \log . a$ at 25°. The $n - \log . \eta$ line can be employed to compare the logarithmic temperature coefficients of tars of different viscosities. In some low-aromatic tars the relationship between $\log . \eta$ and $\log . T°$ F. is given by two straight lines meeting at a single inclination at 30° to 32°. An approximate linear relationship up to 10^5 poises has been found between the loss of oil by distillation and $\log . \eta$. Distillation of the tar in vacuum did not affect the total amount of C1 or the ratio (C1+C2)/C1 (*cf.* p. 407). A similar relationship found for the effect of adding oil to pitch forms the basis for determining the amounts of oil required to produce a specified viscosity. The logarithmic temperature coefficient is also shown to be related to the time-susceptibility of tar in respect of temperature and the relationship may be employed to calculate the change of viscosity for a small change of temperature. When tars of equal viscosity at the same temperature are compared, the logarithmic temperature coefficient $\propto$ time-susceptibility of these tars in respect of viscosity at that temperature.

The work of Evans and Pickard [1] has been applied by Fuidge,[2] Barr [3] and the Standardization of Tar Products Tests Committee [4] to evaluating road tars in terms of equi-viscous temperatures. Fuidge has shown that if some standard viscosity be chosen (within the range of viscosity of road tars at the temperature at which such materials are rolled in road surfacing) the temperature at which the tar has this viscosity is a guide to the temperature of rolling of a road surface dressing for which this particular tar is suitable. Thus the temperature at which a tar has a standard viscosity, known as the equi-viscous temperature, provides a convenient means of characterizing such a tar. A formula connecting the equi-viscous temperature with the time of flow on the B.R.T.A. viscometer, but applicable only when the measured time of flow is not far from the standard time of fifty seconds is: $\theta_1 = \theta + 11 \cdot 5 \, \frac{t-50}{t+50}$, where θ_1 is the equi-viscous temperature in Centigrade degrees, θ the temperature of the test in Centigrade degrees, t the observed time of flow and fifty seconds is the standard viscosity.

Pickard [5] describes a capillary tube form of absolute viscometer and a rotating cylinder viscometer suitable for the determination

[1] *Loc. cit.* [2] *Chem. and Ind.*, 1936, **55**, 301.
[3] *Ibid.*, p. 576. [4] *J. Soc. Chem. Ind.*, 1937, **56**, 422 T.
[5] *The Measurement of the Viscosity of Coal Tars and Pitches*, South Metropolitan Gas Co., London, 1932.

of the viscosity of tar. The " Metro-Trough Viscometer " is shown to give results in close accord with those obtained with an absolute viscometer. The former instrument operates on the principle of the measurement of time of flow of a viscous liquid down an inclined surface. Conversion factors are given to allow of the conversion of viscosity measurements between various technical viscometers. The " Metro-Trough " consistency is multiplied by 7·87 to give the kinematic viscosity. The numerical ratio between consistencies of a number of tars determined with the B.R.T.A. Viscometer and the " Metro-Trough Viscometer " varies between 2·11 : 1 and 1·87 : 1. The average ratio between consistencies determined with the " Metro-Trough Viscometer " and the Hutchinson " Junior " Tar Tester varies between 1·53 : 1 and 1·45 : 1 when the Hutchinson figures are corrected for buoyancy and for density. The observed time on the Hutchinson instrument is multiplied by $\left(\frac{\Delta}{\rho} - 1\right)$, where Δ = apparent density of the float and ρ = density of the liquid. The various tar viscometers are compared with an absolute viscometer, and for a number of different materials it is shown that the deviations from the average correlating factor between the different instruments and the absolute viscometer respectively are :—

	Maximum. Per cent.	Mean. Per cent.
Metro-Trough Viscometer	1·5	1·0
Hutchinson " Junior " Tar Tester (corrected values)	1·0	1·0
Redwood No. 2 Viscometer	1·0	0·5
B.R.T.A. Viscometer	8·0	4·0

Barr and Thorogood [1] conclude that it is not possible to convert Hutchinson times at 25° into B.R.T.A. viscometer times at 30° and this view must be maintained in the present connection, in spite of the publication of alleged correlation charts and systems, which can only be safely applied to pure chemical liquids. The Fuel Research Board has studied the viscosity of pitch over the range 30° to 110° using three different methods, namely, (1) by measurement of a flat disc under load, (2) by use of a rotating cylinder viscometer from 40° to 80° and (3) by use of a capillary tube viscometer above 80°.[2] An instrument somewhat similar to the Hutchinson Tar Tester, namely, the Consistomètre E.P.C., is in use in France, but this falls considerably faster, in a given tar, than the former instrument.

Lee [3] discusses the use of the Ostwald viscometer for measuring the viscosity of tars.

[1] *J. Soc. Chem. Ind.*, 1932, **51**, 381 T.
[2] *Technical Paper*, No. 39, 1933. [3] *J. Soc. Chem. Ind.*, 1934, **53**, 69 T.

3. *Equi-viscous Temperature.* Certain of the considerations mentioned under Viscosity above and relating to the viscosity/temperature characteristics of tars have led to an attempt to devise one scale of measurement which would cover the whole range of viscosities from very thin to very thick tars. As has been stated, it is impossible to draw a relationship between the viscosity at one temperature and that at another, in terms of efflux times in the standard instrument and applicable to all tars within limits of accuracy which would have any practical value ; the same applies to the relationship between the efflux times in the 10 mm. and 4 mm. tar cups. A special Viscosity Panel of the Standardization of Tar Products Tests Committee attempted to avoid the criticisms levelled against the tar viscometer, by ultimately recommending the system which has come to be characterized by the term " Equi-viscous Temperature " (E.V.T.).[1]

The E.V.T. of a tar is the temperature in °C. at which the viscosity is fifty seconds when determined according to the Standard Method, using the standard 10 mm. cup. For practical purposes—in connection with the sale and purchase of tar—the application of this principle of definition has been somewhat modified ; further reference to this point will be found below, following consideration of the " marketing " test.

The method depends on whether the tar has an E.V.T. above or below 17·5° C. ; if the E.V.T. is expected to be above that temperature the viscosity of the tar is determined by the use of the standard 10 mm. cup at a temperature determined as follows :—(*a*) if the specification indicates the temperature of test to be used in determining the E.V.T., that temperature is of course used ; the E.V.T. is obtained by reference to table A ; the correction is applied to the temperature of test. (*b*) If the specification does not indicate the temperature of test, the viscosity is determined at that temperature which is the multiple of 5° nearest to, or 2·5° above the expected E.V.T. If the temperature chosen is the correct one, the viscosity found will lie between 33 and 75 seconds and the E.V.T. can be obtained directly from the temperature of test and the appropriate correction from table A. If the viscosity is outside the range 33 to 75 seconds, the approximate E.V.T. is obtained by using the table and the determination of the viscosity is repeated at the proper temperature, whereafter the E.V.T. is obtained from the result of the repeat determination by reference to the table.

The method for tars of E.V.T. below 17·5° C. is exactly parallel to the foregoing except that the 4 mm. tar cup is used in place of the 10 mm. tar cup, and table B is used instead of table A.

[1] " Standardization of Tar Products Tests Committee," *J. Soc. Chem. Ind.*, 1937, **56**, 422 T. ; *cf.* G. H. Fuidge, *Chem. and Ind.*, 1936, **55**, 301.

A. *Corrections in Centigrade Degrees to be applied to Temperatures of Test, to give E.V.T.s of Tars of Known Viscosity*

Standard 10 mm. Cup

Viscosity in seconds.	0.	1.	2.	3.	4.	5.	6.	7.	8.	9.
10	−10·4	−9·8	−9·2	−8·7	−8·2	−7·7	−7·3	−6·9	−6·5	−6·1
20	− 5·7	−5·4	−5·1	−4·8	−4·5	−4·3	−4·0	−3·8	−3·5	−3·3
30	− 3·1	−2·9	−2·7	*−2·5*	*−2·3*	*−2·2*	*−2·0*	*−1·9*	*−1·7*	*−1·5*
40	*− 1·4*	*−1·2*	*−1·1*	*−0·9*	*−0·8*	*−0·6*	*−0·5*	*−0·4*	*−0·3*	*−0·1*
50	*0*	*+0·1*	*+0·2*	*+0·3*	*+0·5*	*+0·6*	*+0·7*	*+0·8*	*+0·9*	*+1·0*
60	*+ 1·1*	*+1·2*	*+1·3*	*+1·4*	*+1·5*	*+1·6*	*+1·7*	*+1·7*	*+1·8*	*+1·9*
70	*+ 2·0*	*+2·1*	*+2·2*	*+2·2*	*+2·3*	*+2·4*	+2·5	+2·5	+2·6	+2·7
80	+ 2·8	+2·8	+2·9	+3·0	+3·0	+3·1	+3·1	+3·2	+3·3	+3·3
90	+ 3·4	+3·5	+3·5	+3·6	+3·6	+3·7	+3·7	+3·8	+3·9	+3·9
100	+ 4·0	+4·0	+4·1	+4·1	+4·2	+4·2	+4·3	+4·3	+4·4	+4·4
110	+ 4·5	+4·6	+4·6	+4·7	+4·7	+4·8	+4·8	+4·9	+4·9	+5·0
120	+ 5·0	+5·1	+5·1	+5·2	+5·2	+5·2	+5·3	+5·3	+5·4	+5·4
130	+ 5·5	+5·5	+5·5	+5·6	+5·6	+5·7	+5·7	+5·7	+5·8	+5·8
140	+ 5·9	+5·9	+6·0	+6·0	+6·0	+6·1	+6·1	+6·1	+6·2	+6·2

Note.—That part of the table giving corrections for tars having viscosities between 33 and 75 seconds inclusive may alone be used in calculating the E.V.T. to be reported when no temperature of test is stated or implied by a tar specification. The remainder of the table will be useful in ranging tests.

B. *Corrections in Centigrade Degrees to be applied to Temperatures of Test, to give E.V.T.s of Tars of Known Viscosity*

4 mm. Cup

Viscosity in seconds.	0.	1.	2.	3.	4.	5.	6.	7.	8.	9.
20	−33·9	−33·3	−32·8	−32·3	−31·8	−31·3	−30·9	−30·5	−30·1	−29·7
30	−29·4	−29·0	−28·7	−28·4	−28·1	−27·8	−27·5	−27·2	−27·0	−26·8
40	−26·6	−26·3	−26·1	−25·8	−25·6	−25·4	−25·2	−25·0	−24·8	−24·6
50	−24·4	−24·2	−24·0	−23·8	−23·7	−23·5	−23·4	−23·2	−23·1	−22·9
60	−22·7	*−22·5*	*−22·4*	*−22·2*	*−22·1*	*−21·9*	*−21·8*	*−21·6*	*−21·5*	*−21·3*
70	*−21·2*	*−21·1*	*−21·0*	*−20·9*	*−20·8*	*−20·7*	*−20·6*	*−20·5*	*−20·4*	*−20·3*
80	*−20·2*	*−20·1*	*−20·0*	*−19·9*	*−19·7*	*−19·6*	*−19·5*	*−19·4*	*−19·3*	*−19·2*
90	*−19·1*	*−19·0*	*−18·9*	*−18·8*	*−18·7*	*−18·6*	*−18·5*	*−18·4*	*−18·4*	*−18·3*
100	*−18·2*	*−18·1*	*−18·0*	*−17·9*	*−17·8*	*−17·7*	*−17·6*	−17·5	−17·4	−17·3
110	−17·2	−17·1	−17·1	−17·0	−16·9	−16·8	−16·8	−16·7	−16·7	−16·6
120	−16·6	−16·5	−16·4	−16·3	−16·2	−16·1	−16·1	−16·0	−16·0	−15·9
130	−15·8	−15·7	−15·7	−15·6	−15·6	−15·5	−15·5	−15·4	−15·4	−15·4
140	−15·4	−15·3	−15·3	−15·2	−15·2	−15·1	−15·1	−15·0	−15·0	−14·9
150	−14·9	−14·8	−14·7	−14·6	−14·6	−14·5	−14·5	−14·4	−14·4	−14·3
160	−14·3	−14·2	−14·2	−14·2	−14·1	−14·1	−14·1	−14·0	−14·0	−13·9
170	−13·9	−13·8	−13·8	−13·7	−13·7	−13·6	−13·6	−13·5	−13·5	−13·4
180	−13·4	−13·4	−13·3	−13·3	−13·3	−13·2	−13·2	−13·2	−13·1	−13·1
190	−13·0	−13·0	−12·9	−12·9	−12·8	−12·8	−12·8	−12·7	−12·7	−12·6
200	−12·6	−12·5	−12·5	−12·5	−12·4	−12·4	−12·4	−12·3	−12·3	−12·3

Note.—That part of the table giving corrections for tars having viscosities between 61 and 106 seconds inclusive may alone be used in calculating the E.V.T. to be reported when no temperature of test is stated or implied by a tar specification. The remainder of the table will be useful in ranging tests.

Under conditions of standard testing, the results by either part of the method should fall within a fifth of a degree of the average of the several readings. That is not necessarily within a fifth of a degree of the true E.V.T. for, as mentioned earlier, a certain amount of liberty has been taken in the development of an E.V.T. test which can be accepted for general application. The method as applied to tars having E.V.T.s above 17·5° C. may give a result differing by anything up to 10 per cent. from the true E.V.T. If it be required to know the true E.V.T., the viscosity should be determined at two temperatures, differing by at least 5° but not more than 10° C. and such that the viscosities are within the range 25 to 100 seconds. The value of the E.V.T. is calculated for each temperature of test by reference to table A on p. 403. If the same value be obtained, it represents the true E.V.T. If the two values are not identical, the true E.V.T. is calculated by means of the following formula :—

$$\text{True E.V.T.} = T_1 - \frac{d_1}{d_2 - d_1}(T_2 - T_1)$$

where T_1 and T_2 = the values of the E.V.T. calculated from the two test temperatures ; and

d_1 and d_2 = the respective corrections applied to the temperatures of test to give the E.V.T.

If the temperature of test is above the E.V.T., the corresponding value of d is negative.

Example :

Temperature of test	40° C.
Viscosity	30 seconds
Correction, *i.e.* d_1	−3·1° C.
∴ E.V.T., *i.e.* T_1	36·9° C.
Temperature of test	35° C.
Viscosity	73 seconds
Correction, *i.e.* d_2	+2·2° C.
∴ E.V.T., *i.e.* T_2	37·2° C.

$$\therefore \text{True E.V.T.} = T_1 - \frac{d_1}{d_2 - d_1}(T_2 - T_1)$$

$$= 36{\cdot}9 - \frac{-3{\cdot}1}{2{\cdot}2-(-3{\cdot}1)}(37{\cdot}2 - 36{\cdot}9)$$

$$= 37{\cdot}1^\circ \text{ C.}$$

In the case of tars of E.V.T. below 17·5° C., the value of the E.V.T. obtained by the appropriate part of the method (using the 4 mm. cup) may differ from the true E.V.T. by an amount in general not exceeding ±1·0° C. If it be required to know the true E.V.T., it is necessary to determine the viscosity by the method using the standard 10 mm. cup at two temperatures sufficiently low to give viscosities within the

range 25 to 100 seconds. The log of the viscosity is plotted against the log of the temperature in ° F. The points are joined by a straight line and the log of the E.V.T. obtained by interpolation.

4. *Water.* In the Standard Method the Dean and Stark assembly is used; 100 g. of sample is weighed into the distillation flask and 100 ml. of solvent naphtha is added to facilitate distillation. The method then follows the usual lines.

5. *Distillation.* Light oils, boiling below 170° or 200°, should not be present; standard specifications limit the light oil content to 1 per cent. Medium oils (170°, or 200° to 270°) give the tar its fluidity. The quantity is, however, limited by specification, to allow for penetration of the tar into the stone structure of the road, for a certain amount of evaporation of these oils and their resinification due to oxidation and polymerization.

Since the development of Standard Methods for testing road tar in 1929, perhaps the matter of most concern, and certainly one which has been responsible for a considerable amount of practical investigation, has been the difficulty of carrying out the distillation of road tar in the laboratory under practical conditions which represent a really satisfactory measure of control. The resulting technique in the 1938 edition of *Standard Methods* introduces nothing phenomenal by way of apparatus but the method of actual distillation is particularly stringently controlled.

The apparatus consists of a standard distillation flask of 750 ml. distillation capacity fitted with a standard air condenser and thermometer, the flask being placed in a British Standard draught-screen. Weighed Crow receivers are used to collect the distillate and a large-size Bunsen burner is used as the source of heat. A water-gauge connected between the gas-tap and the burner is an advantage in controlling the distillation rate.

750 g. of the tar is weighed into the weighed flask and heated at such a rate that the thermometer indicates 200° C. within 35 ± 5 minutes from the start. When oil commences to distil, the rate of heating is adjusted so that (*a*) 5 ml. of distillate collect in at least 54 but not more than 66 seconds. This distillation rate (which corresponds to 5 ml. $\pm 0 \cdot 5$ per minute) must be strictly maintained throughout the remainder of the distillation, except that (*b*) the collection of the first 5 ml. in any receiver may extend over 75 seconds as the upper limit, and (*c*) if the collection of any 5 ml. extends over less than 54 or more than 66 seconds the collection of 15 ml. including that 5 ml. must extend over at least 165 but not more than 195 seconds. If in any test the foregoing conditions are not met, the test must be discarded and another test carried out with a further portion of the sample.

The time to collect each 5 ml. is kept under close observation and recorded so that compliance with the distillation requirements can subsequently be confirmed. At 200° C. the receivers are changed and the second and subsequent receivers warmed just before use to prevent solids depositing and interfering with the checking of the distillation rate. Subsequent changes are made at the specified temperatures, but it should be noted that in connection with the phenols determination (see sub-section 6 below) a cut at 270° C. is required. The weights of the distillates are determined and an assumed density of unity for the water in the first fraction is used for calculation of the weight of the oil in the first fraction. In anticipation of future specification requirements the Standard Method provides for reservation and appropriate treatment of the residue in the flask to obtain a characterization of the residual pitch by the Ring and Ball test (see p. 420).

As an additional control, the test is carried out in duplicate and the separate results as well as the average reported. Certain easements are provided in the distillation rate requirements to cope with samples which are liable to froth on heating. The barometric pressure is recorded, but in normal circumstances is not to be used for temperature corrections ; referee tests should be carried out when the pressure is within 5 mm. of 760 mm. or temperature corrections must be made.

6. *Phenols.* The phenols content of road tars is limited by specification because of the contamination through rain washings and the consequent harmful effect on fish in neighbouring waters, and on vegetation along the highway. Butterfield [1] discusses at length the subject of toxicity of tar products to fish, and Shelford [2] gives the results of an experimental study of the subject. The Chemical Department of the South Metropolitan Gas Company discuss tests which may be applied to tar products with regard to toxicity.[3]

Other data will be found in the Report of the Ministry of Transport and the Ministry of Agriculture and Fisheries.[4]

For the determination according to the Standard Method the whole of the oil distilling to 270° C. in the distillation test is examined on the usual lines, the phenols being extracted by caustic soda and liberated for measurement by the addition of hydrochloric acid, after the soda washings have been boiled to remove neutral oils and bases.

The method of Fox and Gauge [5] has been applied for the determination of the limited amounts of phenols in non-toxic tars.

7. *Naphthalene.* Naphthalene acts as a diluent, effecting a sensible reduction in the consistency of the road tar.[6] The naph-

[1] *J. Soc. Chem. Ind.*, 1928, 47, 293 T.
[2] *Bull. Illinois State Lab. of Natural History*, March 1917.
[3] *J. Soc. Chem. Ind.*, 1937, 56, 184 T. [4] Dated 14th March 1922.
[5] See p. 298. [6] *Cf.* p. 398.

thalene volatilizes after application of the road tar, and consistency then increases, but if the naphthalene is present in excess, too rapid volatilization may affect adversely the soundness of the tar coating. The naphthalene content of German standard road tars is therefore limited to 3 to 4 per cent. ; British Standard specifications require a naphthalene content not in excess of 3 to 6 per cent. According to the Standard Method the whole of the oil distilling to 270° C. in the distillation test is used after washing with caustic soda solution to remove phenols in the test for those constituents (see 6 above). The method is the usual one of cooling to 15·5° C. and maintaining the material within half a degree of that temperature for two hours with occasional stirring. There is no seeding of the cooled material. The naphthalene is separated on a Buchner funnel fitted with a rapid filter paper and is freed from oil by means of a hand screw-press and then weighed. The " corrected wet crystallizing point " of the pressed naphthalene must not be lower than 70° C. (see crystallizing point test for crude naphthalene, p. 297).

8. *Insoluble Matter (" Free-Carbon ") and Ash.* The significance of the " free-carbon " content of a road tar is not clear.[1] The " free-carbon " forms the dispersed phase in a stable system in which the high-boiling tar oils constitute the dispersing medium. The portion of the free-carbon insoluble in pyridine (C_1) appears to be coarsely dispersed and visible under the ordinary microscope. The portion soluble in pyridine (C_2) appears to be present in the extremely divided state of the ultra-colloid. Mallison [2] considers that the coarse particles of the " free-carbon " give a certain stability to the system, and the more finely dispersed particles determine the adhesive and binding properties of the tar. C_2 appears to be capable of redispersion in tar oils, and then is no longer visible under the microscope. Differences in this respect of C_2 from vertical retort tar and from horizontal retort tar are proposed as an explanation of the fact that a base tar of given consistency from a vertical retort tar requires more oil to produce a road tar of given viscosity than does a base tar of like consistency from horizontal retort tar.[3] The addition of certain petroleum asphalts to the prepared tar disturbs the system, the mixture becomes dull, and a grain effect develops to an extent dependent on the nature of the tar and the added bitumen. In contrast, certain petroleum residues are homogeneously dispersed in road tar. Barash [4] points out that the presence of material of an inert character would seem to affect adversely the binding properties of the tar and its resistance to disintegration ; hence, vertical retort tar should be superior to horizontal retort tar in

[1] *Cf.* p. 399.
[2] *International Conference on Bituminous Coal,* Pittsburgh, 1931, vol. i., p. 947.
[3] Adam and co-workers, *J. Soc. Chem. Ind.*, 1937, 56, 413 T.
[4] *J. Soc. Chem. Ind.*, 1926, 45, 441 T.

this respect. He considers, moreover, that the so-called " free-carbon " from vertical retort tar is a highly agglutinating organic complex, probably similar in composition to the asphaltenes or carbenes obtained from natural bitumens. The latter are very sensitive to the effect of heat ; when maintained at a temperature of 200° for some time, they lose their ready solubility in their associated hydrocarbons, and cease to function as binding agents. " Free-carbon " in a horizontal retort tar is said to give body or extra tenacity to the road tar, but when the tar is applied in thin films the particles of " free-carbon " tend to segregate, absorb moisture, and give rise to serious disintegration.

A fairly wide range of " free-carbon " contents is permitted by the various standard road-tar specifications.

8. *Insoluble Matter ("Free-Carbon") and Ash.* 2 g. of the sample is warmed on the water-bath with 100 ml. of hot pure toluole. After settlement for twenty minutes with the beaker on the boiling water-bath, the supernatant liquid is decanted either through balanced filter papers or a Gooch crucible fitted with asbestos. Washing is effected by repeated decantation until 300 ml. of toluole has been used. The residue is then transferred to the filter and the washing continued until a total of 500 ml. of toluole has been used. The residue is dried to constant weight at 95° to 110° C. After weighing it is incinerated, the weight of the ash deducted (allowing for that in the filter-paper if used) and the percentages by weight of ash-free " free-carbon " and of ash are calculated.

(f) Road Tars Containing Asphalt

Preparations containing asphalt are in common use for road purposes. The quantitative estimation of asphalt in such products depends on the action of concentrated sulphuric acid. Tars give sulphonic acids soluble in water, whereas asphalts and asphaltic bitumens give water-insoluble addition products. Marcusson's method [1] is as follows :—

3 to 4 g. of road tar is weighed into an Erlenmeyer flask and treated for fifteen minutes with ten times its weight of chloroform or carbon disulphide under a reflux condenser. The free-carbon is filtered off and washed with the solvent until the filtrate is practically colourless. The solvent is now removed from the filtrate by distillation and the last traces on the water-bath. 6 to 8 ml. of 95 per cent. concentrated sulphuric acid (double the volume amount of the weight of the tar) is now added to the recovered residue contained in the same Erlenmeyer flask, and the whole placed on a boiling water-bath for

[1] *Die Natürlichen und Kunstlichen Asphalte*, Leipzig, 2nd edn., 1931, pp. 91, 106 ; Mallison, *Verkehrstechnik*, 1928, **8**, 121 ; *D.I.N. Vorschrift*, 1995.

forty-five minutes, stirring meanwhile with a glass rod until sulphonation is completed. The mass is allowed to cool, transferred to a thick-walled glass beaker, crushed, and the sulphonated mixture diluted with 500 ml. of distilled water. After the lapse of at least two hours it is decanted into a weighed filter or Gooch crucible of about 7 cm. diameter ; the residue is washed until the filtrate is no longer acid to methyl orange, dried at 110° and weighed. The weight corresponds for practical purposes to the content of asphaltic bitumen in the tar, especially if it is Mexican asphaltic bitumen.

The range of application of this method is limited to normal asphaltic oil residues and to mixtures containing about 25 per cent. of asphaltic bitumen. The accuracy is about 1 to 2 per cent. of the real value, but with mixtures containing large quantities of asphaltic bitumen the method must be regarded as inaccurate.[1]

Höpfner [2] describes a modification of this method in which sulphonation is effected with ten times the amount of sulphuric acid at a temperature of 107° to 108° for a period of two-and-a-half hours with vigorous mechanical stirring. The solid asphaltic bitumen product is obtained in a granulated easily filterable condition. The quantity so determined is from 15 to 25 per cent. in excess of the true value.

The asphalt content of road tars containing Trinidad asphalt and other mineral-containing natural asphalts may be calculated from the ash content of the original material. In a road tar, however, the mineral matter has a tendency to settle out.

Nellensteyn and Kuipers [3] indicate a method of analysis of road tar-asphalt mixtures involving the use of solvents, and Becker [4] describes the experimental testing of such products by means of ultra-violet light. The latter method is of little value for quantitative estimations.

XI. PITCH

(a) Properties

Coal tar pitch is a resinous mass of a dark black colour with a more or less brilliant conchoidal fracture. Its brittleness varies according to the degree of hardness obtained in the distillation. Its sp. gr. varies from 1·10 in the case of low-temperature tar pitch to 1·35 or even 1·40 in the case of pitch obtained from coke-oven and horizontal retort tars. The commercial products are: Soft pitch,

[1] Mallison, *Asphalt. u. Teer, Strassenbautechnik*, 1930, **30**, 1183.

[2] *Techn. Gemeindeblatt*, 1928, **31**, 94.

[3] *Chem. Weekblad*, 1932, **29**, 291.

[4] *Asphalt u. Teer, Strassenbautechnik*, 1930, **30**, 87 ; see also Teuscher, *Chem. Fabrik*, 1930, **3**, 53.

medium soft pitch and hard pitch, and although these terms may not invariably have the same meaning, the three products, in general, have the following properties respectively: *Soft pitch* softens at 40° and melts at 50°; it is tough at ordinary temperatures, and can be broken up only at a low temperature, and on long standing the fragments coalesce. The fractured surface shows a brilliant lustre. If left exposed to the sun it soon flows, forming a viscous mass with a mirror-like surface.

Medium pitch (briquette pitch) softens at 60° and melts at about 70°; it is solid at ordinary temperatures and is easily broken into fragments which, however, rarely show sharp edges. It soon forms a shapeless mass if exposed to sunshine.

Hard pitch begins to soften at 80° to 85° and melts between 95° and 120°. When broken up it forms sharp-edged resonant fragments of dull lustre which are little affected by exposure to the sun.

The softening points of three different kinds of pitch, together with the mean specific heats, are given below [1]:—

	Softening point. Ball-and-ring method. °C.	Mean specific heat. Gramme-calories/gramme/°C.	
		20° to 50° C.	20° to 85° C.
A. Pitch from vertical retort tar from Durham coal carbonized in Glover-West retorts. Tar distilled to 360° without steam .	53	$0{\cdot}32_9$	$0{\cdot}34_6$
B. Medium soft pitch from horizontal retort tar from Durham coal. Tar distilled and distillation completed with steam at 300° to 320°	60	$0{\cdot}33_3$	$0{\cdot}34_1$
C. Pitch from low-temperature tar. Tar distilled to 310° without steam . . .	44	$0{\cdot}41_7$	$0{\cdot}40_8$

The fact that the mean value for pitch C between 20° and 85° is lower than the value between 20° and 50° is explained as being due to the fact that this pitch has a softening point below 50°, and latent heat is absorbed in the lower range of temperatures in melting the pitch. In the case of the first two samples the latent heat of fusion is supplied at a temperature higher than 50°.

Small amounts of other types of pitch are obtained as by-products in the refining of coal-tar derivatives, principally in Germany. Anthracene pitch, obtained as a residue in the distillation of anthracene, is a hard, black, glossy material; naphthol pitch, produced in refining of β-naphthol or naphthylamine,[2] is a glossy black solid with a fusion-

[1] *Annual Report of the Fuel Research Board*, 1928; *Technical Data on Fuel*, London, 1930, p. 86.

[2] Grempe, *Farben-Zeitung*, 1915, **26**, 322; G.P. 302741 and 302742, 1916.

point of about 120° and almost completely soluble in xylole, chloroform and pyridine ; cresol pitch, known variously as Karbolpech, Kresolharz and Phenolpech, obtained in the distillation of crude cresol has a fusion-point of 60° to 80°, and is more or less soluble in aqueous potassium hydroxide and almost completely soluble in alcohol and mixtures of alcohol and benzole.[1] None of these is an article of commerce in Great Britain.

Church and Weiss[2] determined the properties of representative specimens of coal tar pitch as indicated in the following table :—

	Gas works pitch.			Coke-oven pitch.		Scotch blast-furnace pitch.
	Horizontal retorts.	Inclined retorts.	Vertical retorts.	Otto-Hoffman coke-ovens.	Semet Solvay coke-ovens.	
Specific gravity at 60° F./60° F.	1·30	1·28	1·19	1·25	1·25	1·23
Hardness at 115° F.	Too soft	Too soft	Too soft	Too soft	Too soft	324
„ „ 77° F.	39	40	44	41	39	41
„ „ 32° F.	2	2	2	3	2	8
Fusing point (cube method) °F.	125	123	125	126	126	135
Fixed carbon, per cent.	41·5	37·0	16·3	28·5	28·2	14·4
Soluble in carbon disulphide, per cent.	64·9	67·8	89·5	79·9	82·5	58·2
Non-mineral matter, insoluble, per cent.	34·9	32·0	10·3	19·7	17·4	30·0
Mineral matter, per cent.	0·2	0·2	0·2	0·4	0·1	11·8
Carbenes, soluble in carbon disulphide but insoluble in carbon tetrachloride	3·5	2·8	5·3	7·4	5·9	2·6
Free-carbon, per cent.	34·9	30·8	8·0	21·1	18·3	28·4

Abraham also gives extensive data on the properties of various types of coal tar pitch.[3] Numerous investigations have been made of the elementary composition of pitch, but no relation has been found to exist between composition and hardness. Characteristic analyses are given below :—

	Soft pitch. Per cent.		Medium hard pitch. Per cent.		Hard pitch. Per cent.	
	*a.**	*b.*†	*a.**	*b.*†	*b.*†	*c.*‡
Carbon	91·60	91·80	85·14 to 92·59	94·32	93·16	75·32
Hydrogen	4·89	4·62	4·85 „ 4·60	2·98	4·36	8·90
Oxygen, nitrogen and sulphur	3·20	...	7·87 „ 2·77	...	...	16·06
Ash	0·31	...	2·54 „ 0·04	...	...	0·43

* Constam and Rougeot, *Glückauf*, 1906, **42**, 489.
† Donath and Asriel, *Chem. Rev. Fett. Ind.*, 1903, **10**, 54.
‡ Habets, *cf.* Guelt, *Steinkohlenbriquette*, p. 23.

[1] Mallison, *Zeit. Teer*, 1924, **22**, 27.
[2] *Proc. Amer. Soc. Testing Materials*, 1915, **15**, Part II., 274.
[3] *Asphalts and Allied Substances*, London, 1938, p. 371.

The sulphur content of a number of samples of gas works pitch varied between 0·45 and 0·49 per cent.[1]

According to the investigations of Constam and Rougeot [2] the heat of combustion of pitch varies from 8100 to 8900 cals., and its net calorific value from 7850 to 8650 cals.

If heated in an open crucible, pitch melts and intumesces, giving off yellow vapours which have a pungent odour, while a porous coke remains. The quantity of coke from high-temperature tar pitches may vary between 30 and 60 per cent.

Coal tar pitch is more or less readily soluble in the usual solvents, less readily soluble in methyl and ethyl alcohols, readily soluble in ether and light petroleum, very readily soluble in chloroform, carbon disulphide and benzene and most completely and quickly soluble in aniline and in the mixture of pyridine bases. These solutions are either brown or black, and exhibit, in reflected light, the characteristic property of bluish-green fluorescence of different shades of colour, according to the solvent employed.[3] A more or less considerable carbonaceous residue remains undissolved, which is the so-called free-carbon (from low-temperature tar pitch, 2 to 25 per cent., from vertical retort and coke-oven tar pitch, 5 to 25 per cent. and from horizontal retort tar pitch 25 to 40 per cent.). The composition of the free-carbon from high-temperature coal tar pitch is, according to Behrens [4] and also Donath and Margosches,[5] as follows :—

	Behrens.		Donath and Margosches.
	I.	II.	
	Per cent.	Per cent.	Per cent.
Carbon	90·84	91·92	89·20
Hydrogen . . .	3·06	3·16	2·30
Nitrogen . . .	...	...	0·70
Ash	0·40	0·87	0·67

(b) Composition

Pitch consists of the non-volatile substances (free-carbon, ash) and the most difficultly volatile substances contained in the tar.

[1] *Alkali Inspector's Report for* 1931, p. 25, London, 1932.
[2] *Glückauf*, 1906, **42**, 489.
[3] *Cf.* p. 88.
[4] *Dingl. polyt. J.*, 1873, 208, 371.
[5] *Chem. Ind.*, 1904, **27**, 220; *J. Soc. Chem. Ind.*, 1904, **23**, 541.

Bituminous constituents which decompose on distillation are also present. Carnelley[1] isolated two distinct bitumens of pitch-like appearance, of which one boiled at 427° to 439° and was readily soluble in benzene and carbon disulphide, while the other distilling above 439° was hardly soluble in benzene, but more readily soluble in carbon disulphide.

Besides the above substances, pitch contains anthracene, phenanthrene, chrysene, pyrene, acridine, etc., which can be separated by distillation, when the bituminous constituents of the pitch undergo partial decomposition with the formation of viscous heavy oils and red resinous substances. A ruby red resinous distillate containing these substances, known as "pitch resin," which melts between 40° and 100° and has a sp. gr. above 1·22, is produced in the distillation of pitch for pitch coke.

(*c*) The Working up of Pitch

In most cases the tar is distilled for a hard pitch in order to recover as much as possible of the more valuable oils. The further working up of pitch consists in adjusting it for medium or soft pitch (cut-back coal tar pitch), or in manufacturing therefrom prepared (regenerated) tar, by adding oil distillation residues ; this product is used for various purposes (roofing composition, steel works tar, etc.), and is made up according to requirements with a certain specified melting-point, sp. gr., consistency, etc.

(*d*) Uses

The most important use of pitch is as a binding material in the manufacture of briquettes ; large quantities are also used for the manufacture of prepared tars, particularly for road purposes and for use in the tar-felting industry.

According to Spilker, a good pitch for the manufacture of briquettes should not contain more than 0·5 per cent. of ash, the softening point (determined by the Kraemer and Sarnow method) should not be below 60° nor above 75°, from 70 to 75 per cent. should dissolve in aniline or pyridine bases, and the coking residue should not exceed 45 per cent. The binding power and elasticity of pitch, for which at present there are no generally accepted tests, are the main factors which determine the value of pitch for briquetting purposes. The resistance to the weather must also be considered if the pitch is required for road making. Taylor[2] describes tests carried out on pitch-sand briquettes to determine more precisely the suitability of pitch for the former purpose. This subject is also discussed by

[1] *J. Chem. Soc.*, 1880, **37**, 714 ; *cf.* Kraemer, *Ber.*, 1903, **36**, 645.
[2] *J. Soc. Chem. Ind.*, 1926, **45**, 417 T.

Property.	1. High carbon coal tar pitch for use below ground level.	2. High carbon coal tar pitch for use above ground level.	3. High bitumen coal tar pitch for use below ground level.	4. High bitumen coal tar pitch for use above ground level.	5. High carbon coal tar pitch for use in built-up roofs.	6. High bitumen coal tar pitch for use in built-up roofs.	7. Coal tar pitch for stone block filler.
Nature	Homogeneous	Homogeneous	Homogeneous	Homogeneous	Homogeneous	Homogeneous	...
Water	Less than 0·0 per cent.	Less than 0·0 per cent.	Less than 0·0 per cent.	Less than 0·0 per cent.	Less than 0·0 per cent.	Less than 0·0 per cent.	Less than 0·0 per cent.
Specific gravity (25°)	1·24 to 1·34	1·25 to 1·35	1·21 to 1·30	1·22 to 1·31	1·25 to 1·34	1·22 to 1·32	...
Softening point (cube-in-water method)	43·3° to 60·0°	54·4° to 68·3°	43·3° to 60·0°	54·4° to 68·3°	60·0° to 65·5°	60·0° to 65·5°	46·0° to 57·0°
Distillation—							
Total distillate, 0° to 300°	Not more than 12·0 per cent.	Not more than 10 per cent.	Not more than 15 per cent.	Not more than 12 per cent.	Not more than 12 per cent.	Not more than 12 per cent.	Not more than 14 per cent.
Residue	Not less than 88 per cent.	Not less than 90 per cent.	Not less than 85 per cent.	Not less than 88 per cent.	Not less than 88 per cent.	Not less than 88 per cent.	Not less than 86 per cent. (softening point not above 75°)
Specific gravity (38°/25°) of total distillate to 300°	Not less than 1·03	Not less than 1·03	Not less than 1·03	Not less than 1·05	Not less than 1·03	Not less than 1·03	Not less than 1·02
Ductility at 25°	Not less than 50 cm.	Not less than 20 cm.	Not less than 50 cm.	Not less than 20 cm.	Not less than 50 cm.	Not less than 50 cm.	Not less than 50 cm. (at 50 to 100 penetration)
Solubility in carbon-disulphide—							
(*a*) insoluble	25 to 35 per cent.	22 to 37 per cent.	...	...	22 to 35 per cent.	...	...
(*b*) soluble (total bitumen)	...	...	75 to 90 per cent.	73 to 88 per cent.	...	78 to 85 per cent.	65 to 80 per cent.
Ash	...	...	...	...	Not more than 0·5 per cent.	Not more than 0·5 per cent.	...

[1] D 42-36 T.
[2] D 145-36 T.
[3] D 200-36 T.
[4] D 201-36 T.
[5] D 251-36 T.
[6] D 252-36 T.
[7] D 112-30, *American Society for Testing Materials, Standards*, 1936, ii. 1019.

D 42-36 T, D 145-36 T, D 200-36 T, D 201-36 T, D 251-36 T and D 252-36 T reverted to tentative status.

Spilker and Born.[1] The roof-felt industry requires a specially penetrative type of pitch as an impregnation material in the preparation of roof felt and as an adhesive (*cf.* p. 378).

The American Society for Testing Materials issues standard specifications for coal tar pitch suitable for use in damp-proofing and water-proofing below and above ground level, for use in constructing built-up roofs surfaced with slag or gravel and as stone block filler. The main features of these specifications are incorporated in the table on p. 414.

All the above tests must be carried out in accordance with the specified methods of the American Society for Testing Materials.

(*e*) Methods of Examination

The testing of coal tar pitch commonly comprises the determination of the sp. gr.; the softening temperature on one or other of the scales represented by the Twisting Test, Kraemer and Sarnow Test, Ring and Ball Test and Half-Inch Cube Test; volatile matter, insoluble matter and ash. The volatile matter content is the complement of the coke residue, the method of test being the same. The determination of the hardness of pitch is frequently required, but much less in the United Kingdom than abroad. Finally, it is occasionally necessary to distinguish, as far as possible, coal tar pitch of different origins, and to detect the presence of natural asphalts.

1. **Specific Gravity.**—The sp. gr. is ascertained by any one of the recognized Standard Methods, but the bottle method is obviously indicated for a solid which, by the procedure for sampling, is necessarily in small pieces. A sample of pitch which has been properly taken will consist of material passing a ¼-in. mesh sieve; normally, such material will be used as received, but in special cases it may be necessary to reduce the sample to powder form in order that all air cavities (which are particularly in evidence in hard pitch) may be eliminated.

A British Standard density bottle having a nominal capacity of 100 ml. is convenient as, in particular, the minimum internal diameter of the neck is such that "¼-in. pitch" will readily pass through into the bottle. The method is in line with that for the determination of sp. gr. in the case of road tar (see p. 393), partly filling the bottle, and when filling up with water, taking care that any entangled air bubbles are removed before the final adjustment.

2. **Softening or Melting of Pitch.**—The softening and melting of pitch do not take place at definite temperatures; on a rising temperature the material gradually changes from a brittle or viscous material to a softer and less viscous substance. Determinations relating to the

[1] *Brennstoff-Chem.*, 1930, 11, 15, 307.

softening or melting of pitch must therefore necessarily be made by empirical methods which are all the more closely defined and must be strictly adhered to if the results are to be truly comparable. Four methods of test have in commercial practice come to be related to the softening or melting of pitch with increase in temperature, though the methods do not constitute determinations of precisely the same characteristic or group of characteristics and little can be done to correlate the tests among themselves. Mention must be made of work done in recent years to correlate one or the other of these tests with the viscosities of tars, as a first step towards the practical change-over to a system which will enable an appropriate temperature-sensitive characteristic of tars and pitches to be lined up on a common scale. The work is not complete.[1]

FIG. 58.—Twisting Test for Pitch—Assembled Apparatus.

The four tests at present employed alternatively to measure the softening or melting of pitch are the Twisting Test, the Kraemer and Sarnow Test, the Ring and Ball Test, and the Half-Inch Cube Test. The Standard Method for each is described below.

(a) *Twisting Test.* The apparatus is that described by Frankland Taylor,[2] and replaces the old practice of twisting a length of pitch between the fingers under water, the temperature of which is gradually raised. Since the introduction of the apparatus illustrated in Fig. 58, it has been possible to make twisting tests, the results of which are strictly comparable; with the former hand method individual operators became amazingly expert and reliable, but no serious attempt could be made to compare strictly the results of independent operators.

The sample of pitch is melted in a special pitch-melting bath and the rectangular rods of pitch are formed in the pitch mould shown in Fig. 59. One of the prisms is fitted into the sockets of the Frankland Taylor apparatus and the assembly completed, with water at 20° C. in the beaker and reaching to a point at least 25 mm. above the upper socket. After a steady temperature has been attained, heat is applied

[1] Fuidge and Deadman, *J. Soc. Chem. Ind.*, 1937, **56**, 427 T.; see also p. 399.

[2] *J. Soc. Chem. Ind.*, 1926, **45**, 423 T.; *cf.* Reeve and Yeager, *Proc. Amer. Soc. Testing Materials*, 1925, **25**, II. 385.

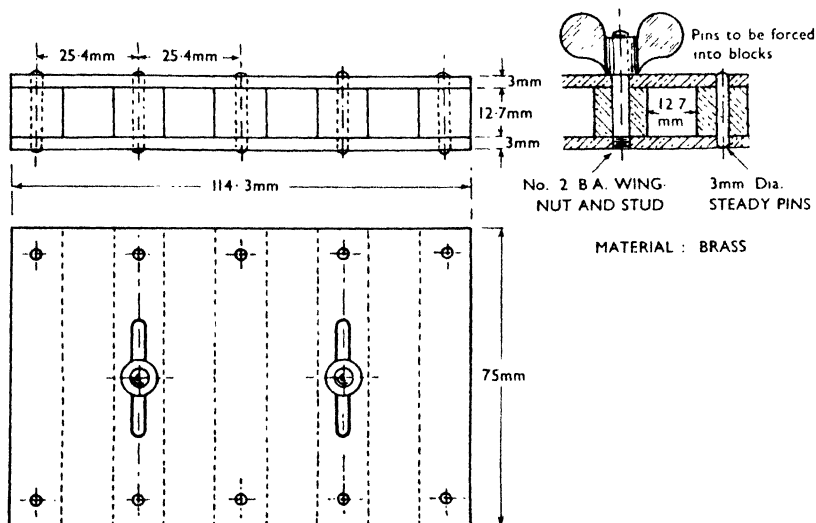
so that the temperature rises 2° in each minute; any test in which, in any half-minute period, the rate of temperature rise is outside the limit of five seconds for a thirty seconds rise for each degree, must be rejected. The torsion is applied when the temperature starts to rise, by allowing the weight to hang freely; the pointer is at the same time set to the zero mark on the scale. The temperature at which the pointer indicates 180 degrees rotation is reported as the result. It is advisable to carry out the test in duplicate.

The dimensions are approximate, except those shown as 12·7 mm., which must be adhered to within ±0·05 mm.

FIG. 59.—Twisting Test for Pitch—Pitch Mould.

(b) *Kraemer and Sarnow Test.* The Standard Method prescribes the apparatus shown in Fig. 60. In respect of both the apparatus and the method the original proposals of Kraemer and Sarnow [1] were modified by Barta [2] and the Standardization of Tar Products Tests Committee itself; in its present standard form, the method gives extremely reliable and consistent results.

The pitch containers, which are short lengths of brass or stainless steel tubing, are filled with molten pitch, which is allowed to overflow. On cooling the excess pitch is removed and the filled containers are attached to the mercury containers (lengths of glass tubing) by means of rubber tubing. 5 g. of mercury is delivered into each of the mercury containers, using one or other of the measures shown in Figs. 61 and 62; these measures are designed to deliver 5 g. of mercury within a maximum tolerance of 0·05 g.

360 ml. and 200 ml. of water at a temperature at least 30° below

[1] *Chem. Ind.*, 1903, **26**, 55. [2] *Petroleum*, 1911-12, 7, 158.

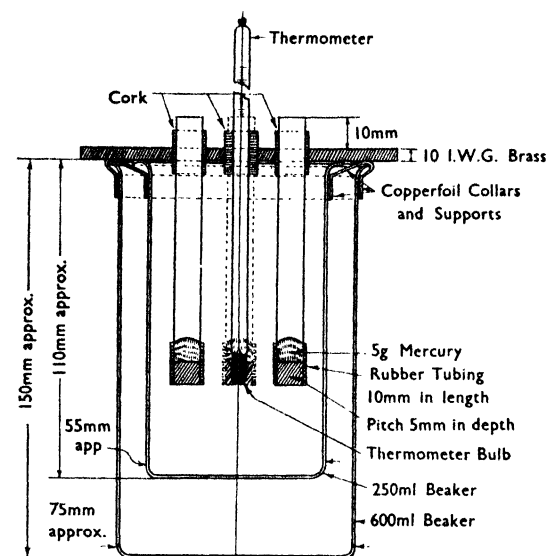



FIG. 60.—Kraemer and Sarnow Test for Pitch—Assembled Apparatus.

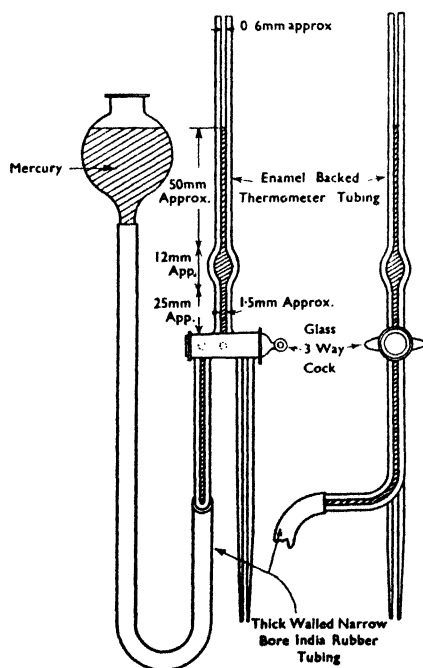



FIG. 61.—Kraemer and Sarnow Test for Pitch—Mercury Pipette.

the expected result are placed in the larger and smaller beakers respectively and the assembly of the apparatus is completed. When temperature equilibrium has been reached, heat is applied so that the temperature rises 2° in each minute. After at least 20° below the expected result, the rate of rise of temperature must be maintained within the limits thirty seconds ±1 for each degree rise. Any tests in which this restriction is not complied with must be rejected.

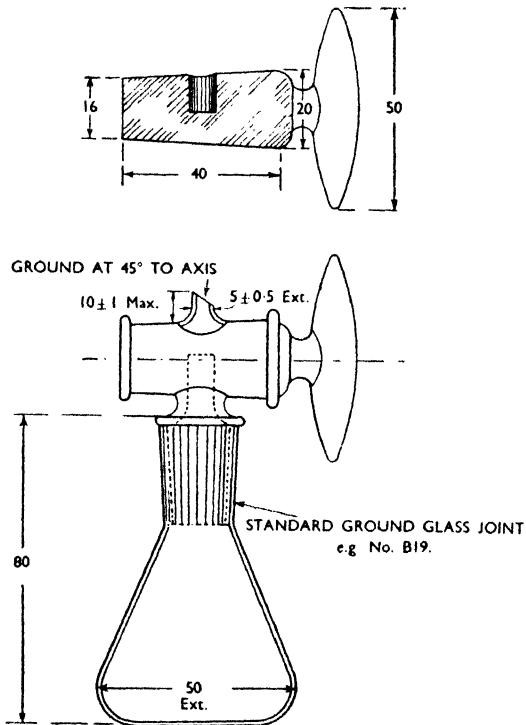
The temperature to be reported is that at which the mercury bursts through the envelope of viscous pitch ; if the envelope of pitch reaches

Where not provided with tolerances, dimensions are intended for guidance.

Fig. 62.—Kraemer and Sarnow Test for Pitch—Alternative Mercury Measure.

the bottom of the beaker without bursting, the temperature at which it is midway between the glass tubes and the bottom of the beaker is reported.

Glycerine is used in the beakers when testing pitches giving results above 80° C. With pitches testing up to 100° C. results should fall within 0·5° C. of the average ; the limit of accuracy is 1° C. for pitches testing between 100° and 120° C.

The method is in common use on the Continent, but is there modified in various particulars. The apparatus is generally of a more elementary design and the rate of temperature rise is not necessarily

that used in British practice (2° per minute). Spilker's[1] modification, using a smooth type-metal rod in place of the mercury, is at first sight a convenience and might commend itself for routine internal works' tests, but it has not been accepted for incorporation in any standard method.

(c) *Ring and Ball Test.* The ring and ball test has long been in use in America, particularly for use in the examination of asphaltic and bituminous products.[2] It has come into favour in recent years in

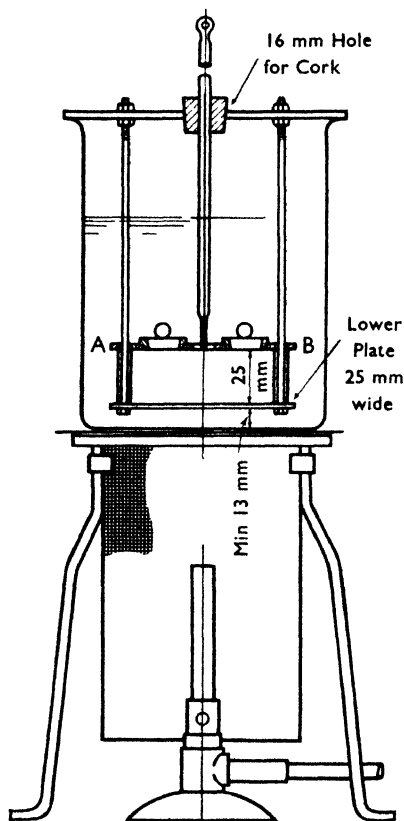



FIG. 63.—Ring and Ball Test for Pitch—Assembled Apparatus.

the United Kingdom for the testing of coal tar pitch and *Standard Methods* 1938 has adopted it with a minor simplifying modification of the apparatus and the use of a thermometer of the British series, but graduated for total immersion in order that the results of the test may be strictly comparable with those obtained when the American technique is followed. The method is finding increasing application on the Continent.

[1] *Z. angew. Chem.*, 1929, **42**, 263.
[2] D 36-26, *Amer. Soc. Testing Materials Standards*, 1936, **2**, 1098.

The apparatus is shown in Figs. 63 to 66. The warmed pitch rings are filled in a manner similar to that used for the Kraemer and Sarnow test except that a minimum excess of pitch is used. The excess is of course removed after cooling.

600 ml. of water is placed in the beaker, the rings put in their support and the support placed concentrically in position. The balls are placed in the beaker (not on the pitch) and the level of the water adjusted so that it is at least 51 mm. above the top of the pitch rings.

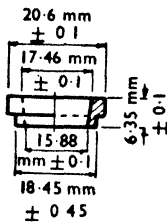



Fig. 64.—Ring and Ball Test for Pitch —Pitch Ring.

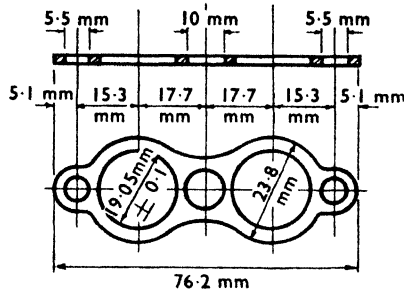



Fig. 65.—Ring and Ball Test for Pitch —Ring Support.

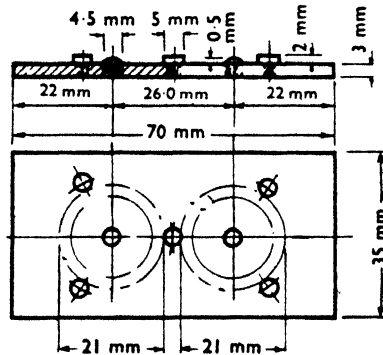



Fig. 66.—Ring and Ball Test for Pitch—Moulding Plate.

The apparatus is allowed to stand for fifteen minutes at a temperature at least 45° below the expected result. The balls are then lifted by means of tongs and placed in the central indentations in the pitch in the rings. Heat is applied at such a rate that the temperature rises 5° in each minute ; after the first three minutes this rate must not be departed from by more than half a degree in any minute and any tests in which the tolerance is exceeded must be rejected.

The temperature at which the pitch surrounding the steel ball first touches the lower plate of the support is reported. No correction is made for the emergent stem of the thermometer. The results of repeat

determinations should fall within half a degree of the mean when that does not exceed 100° C., and within one degree of the mean when the readings exceed 100° but do not exceed 120° C. Glycerine replaces

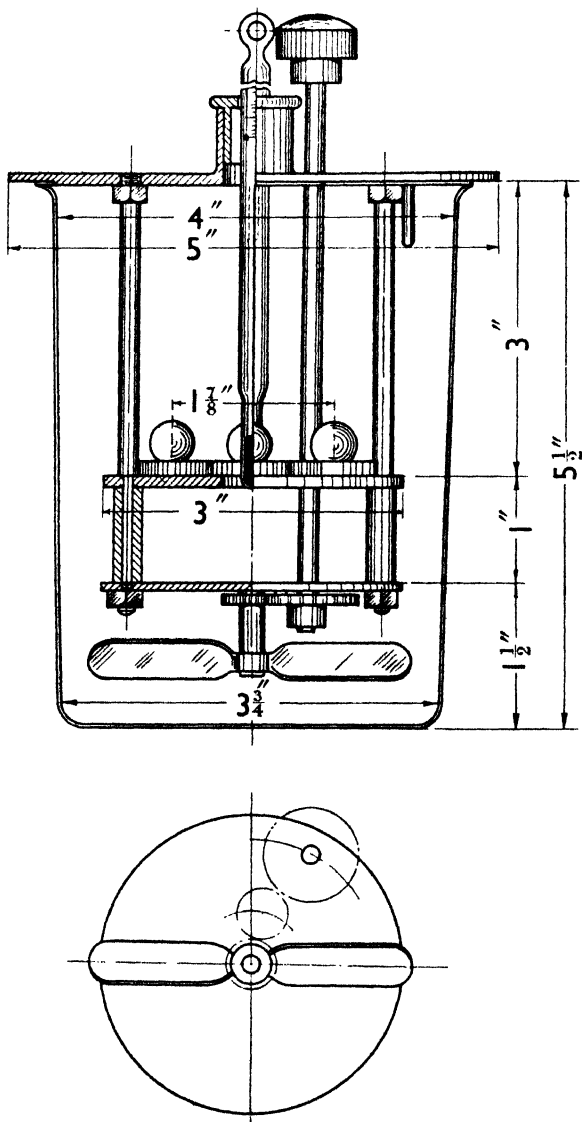



FIG. 67.—Ring and Ball Test for Pitch—Assembled 6-ring Apparatus and Arrangement of Stirring Gears.

the water in the beaker when the result of the test is expected to exceed 80° C. The 6-ring apparatus shown in Fig. 67 will be found useful in laboratories where many samples are to be tested, and is known to

give results within sufficiently practical agreement with those of the 2-ring instrument, for routine working.

(d) *Half-Inch Cube Test.* This test has long been in use in the United Kingdom, and is commonly used in America [1] for the determination of the softening of pitch. The apparatus is shown in Fig. 68. Half-inch cubes of pitch are formed in the mould shown in

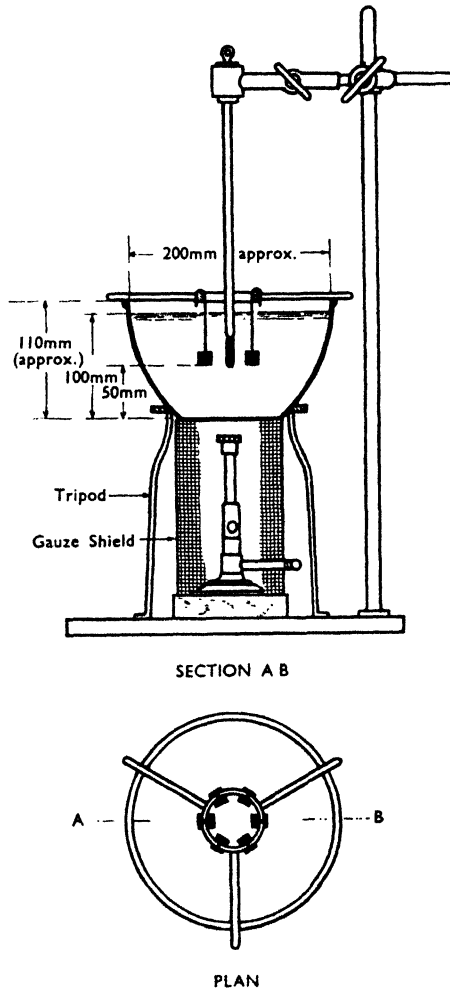



Fig. 68.—Half-inch Cube Test for Pitch—Elevation and Plan of Assembled Apparatus.

Fig. 69 and are mounted on pieces of copper wire. This is done by heating the wire in a glass or metal tube placed in a bath of oil at 200° to 250° C. and passing the hot wire through the centres of two opposite faces of one of the cubes, the end being adjusted precisely

[1] D 61-24, *Amer. Soc. Testing Materials Standards*, 1936, 2, 1103.

flush with the lower face. The bowl is filled with water at 25° C. and when all the cubes have been mounted and placed in position the assembled apparatus is allowed to stand until temperature equilibrium is reached. It is then heated so that the temperature rises 2° per minute; the rate is maintained within the limits thirty seconds ±5 for each °C. after at least 20° below the expected result. If in any minute period the rate falls outside the limits, the test must be rejected.

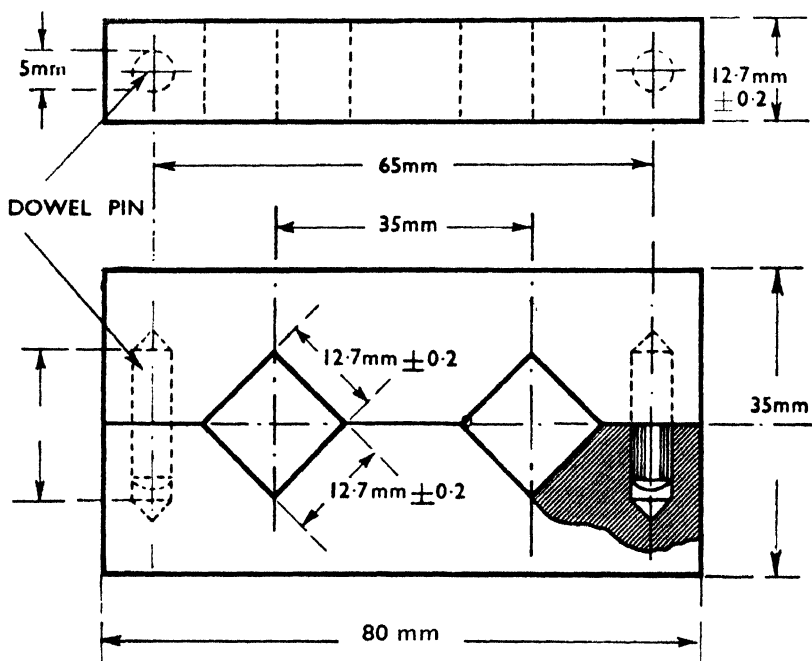
The temperature at which the pitch touches the bottom of the bowl is reported; results from repeat determinations fall within

The dimensions other than 12·7 mm. ±0·2 are for guidance.

FIG. 69.—Half-inch Cube Test for Pitch—Pitch Mould.

half a degree of the average if the Standard Method is strictly complied with, but it should be noted that the upper limit of the test for reliable results is somewhere between 85° and 90° C.

The American Society for Testing Materials standard cube-in-water method for the determination of the softening point of tar products[1] is substantially as the above, except that the cube of pitch is of 12·7 mm. (½ in.) edge; it is suspended with the wire (12 B and S gauge) in the form of a hook entering the cube at right angles to the face; the rate of rise of temperature is 5° per minute and the precise position of the cube in the bath is somewhat different.

[1] *Cf.* Church, *Ind. Eng. Chem.*, 1911, **3**, 230; 1913, **5**, 195.

Evans and Pickard[1] have shown that pitch, even at atmospheric temperatures, behaves as a true viscous fluid, and not as a plastic solid. The "Metro Plastimeter" (Fig. 70) enables the rate of flow of pitch under heavy loads to be measured. In principle a sphere of steel attached to a supporting rod is forced by the application of a suitable weight into a mould of the material under examination, the rate of penetration being measured by observation of the depth of penetration at various times. The rate of flow of pitch varies directly with the force causing the flow, and the relationship between time of penetration and the applied load is strictly linear. The results obtained with this Metro Plastimeter are closely related to those obtained with the Metro-Trough Viscometer (p. 401); the slopes of the logarithmic temperature-consistency curves are practically identical. Hence the determination of the characteristics of pitch by means of the Metro-Trough Viscometer defines the temperature-consistency characteristics over a wide temperature range (60° to 200° F.). Results obtained with the Metro-Trough Viscometer for several samples of pitch of varying degrees of softness and of different origin have been correlated by Pickard,[2] with their softening points determined by the Kraemer and Sarnow, the Half-Inch Cube, and the Ring and Ball methods. The two former series of tests were carried out according to the respective Standard Method, and the latter tests as specified in *Standard Methods for Testing Petroleum and its Products*. The results obtained are tabulated below and shown in graphical form in Fig. 71.

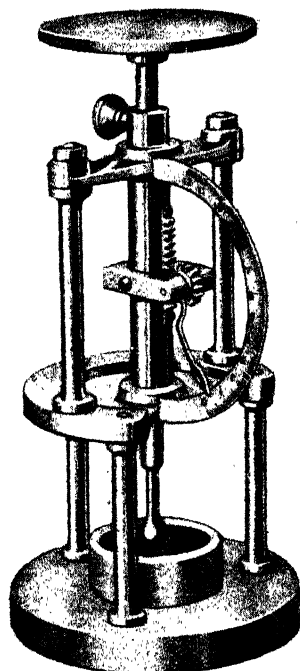



FIG. 70.

Softening point determinations by the Kraemer and Sarnow method fall approximately on an iso-viscous line of the Metro-Trough Viscometer scale; softening point determinations by the Ring and Ball method fall approximately on an iso-viscous line of the Metro-Trough Viscometer scale; fusion point determinations by the Half-Inch Cube

[1] *An Investigation into the Nature and Properties of Coal Tar*, South Metropolitan Gas Co., London, 1931.

[2] *The Measurement of the Viscosity of Coal Tars and Pitches*, South Metropolitan Gas Co., London, 1932.

ORIGIN OF PITCH.
VERTICAL RETORT
HORIZONTAL RETORT A.
COKE OVEN
HORIZONTAL RETORT B.
" " F.
WATER GAS
HORIZONTAL RETORT C.
" " E.
" " D.
K AND S
½" CUBE
RING AND BALL
LOG. TIME (SECONDS)
LOG TEMPERATURE (°F)
0·6
0·8
1·0
1·2
1·4
1·6
1·8
2·0
2·2
2·4
2·6
2·8
3·0
3·2
3·4
3·6
3·8
4·0
2·40
2·30
2·20
2·10
2·00
1·90

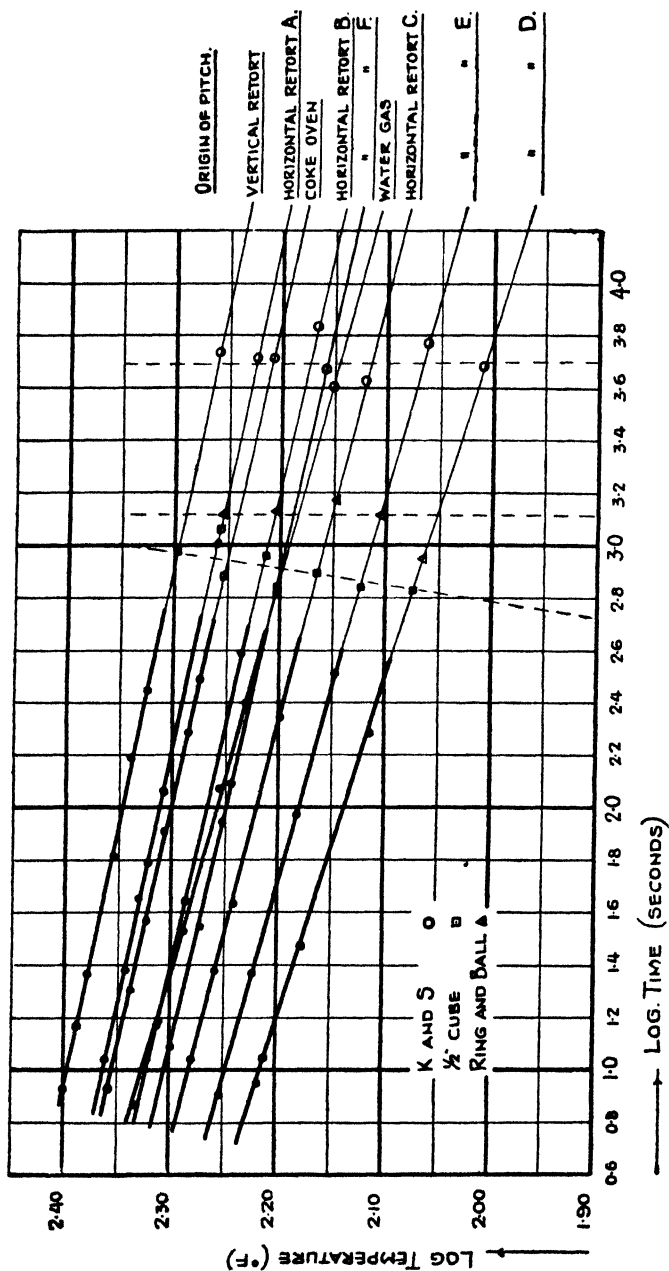



FIG. 71.

Material.	Metro-Trough Viscometer.		Softening point °C.		
	Log. T when log. C=1·0.	Log. T when log. C=2·0.	Kraemer and Sarnow.	Ring and Ball.	Half-Inch Cube.
Horizontal retort pitch A .	2·362	2·311	75·2	82·0	82·4
" " " B .	2·322	2·267	63·5	71·0	73·0
" " " C .	2·281	2·220	54·9	60·2	63·5
" " " D .	2·214	2·138	39·0	46·7	48·1
" " " E .	2·247	2·180	46·1	53·0	56·0
" " " F .	2·305	2·250	61·7	...	71·0
Vertical retort pitch . .	2·396	2·346	82·7	...	92·0
Coke-oven pitch . . .	2·353	2·300	72·2	...	81·5
Water-gas pitch . . .	2·324	2·258	60·7	...	71·0

method fall on a line which is inclined to the log. temperature axis on the Metro-Trough Viscometer scale. From measurements of the viscosity of pitch on a modified twisting cylinder apparatus, similar to that standardized by Taylor,[1] Pickard [2] has shown that the viscosity of a horizontal retort pitch does not vary with wide variations in the rate of shear.

Fuidge and Deadman have examined the extension to pitches of the equi-viscous system which has been introduced for refined tars.[3]

(3) **Volatile Matter.**—The content of volatile matter in pitch has become important and there are signs that it will become an even more critical characteristic. Special attempts were therefore made to ensure that the method in the 1938 edition of *Standard Methods* should be thoroughly reliable and beyond criticism.

The apparatus is shown in Figs. 72 to 74. The Meker burner has a diameter of 31 mm. at the top and gives a flame diameter of 30 mm. A water manometer is fitted between the gas tap and the burner. The apparatus is protected from draughts by a standard semi-cylindrical draught screen.

With the apparatus assembled as shown in the figure but without the crucible lid in position, a small quantity of powdered potassium chromate, spread over the bottom of the crucible, is heated with the flame of the burner fully aerated. The gas pressure is slowly increased until incipient fusion of the chromate is apparent. The manometer reading at this rate of heating is noted.

The crucible is cleaned and weighed; 1 g. of the finely divided sample is weighed into it and, with the lid in position, the crucible is placed in the crucible support. The gas is relit and the pressure adjusted to that noted in the preliminary trial in terms of the manometer reading. The burner is placed under the crucible and after three minutes the flame is extinguished. The crucible is allowed to cool and is weighed without the lid.

[1] p. 416. [2] *Loc. cit.* [3] *J. Soc. Chem. Ind.*, 1937, 56, 427 T.

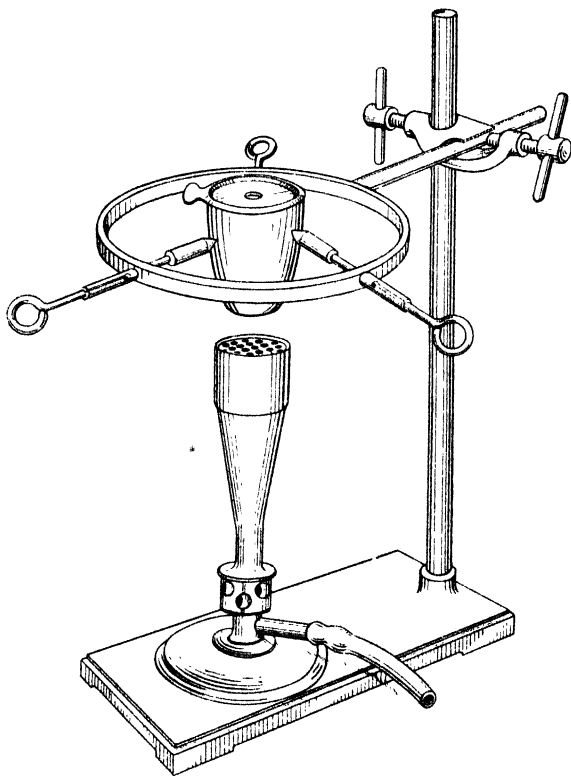



Fig. 72.—Volatile Matter in Pitch—Assembled Apparatus.

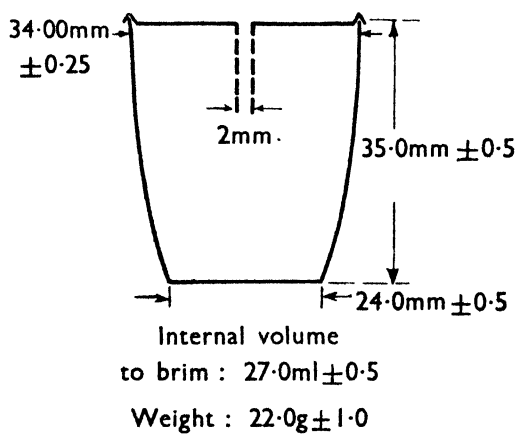



Fig. 73.—Volatile Matter in Pitch—Platinum Crucible and Lid.

The results of repeat determinations should fall within half a unit of the average. If there is any evidence that molten pitch has spurted on to the lid, the test must be discarded and a fresh determination made.

In America it is the practice to declare the fixed carbon, that is to say, the percentage of the pitch which remains in the crucible less the percentage of ash ; the volatile matter is spoken of as the " volatile combustible matter." [1]

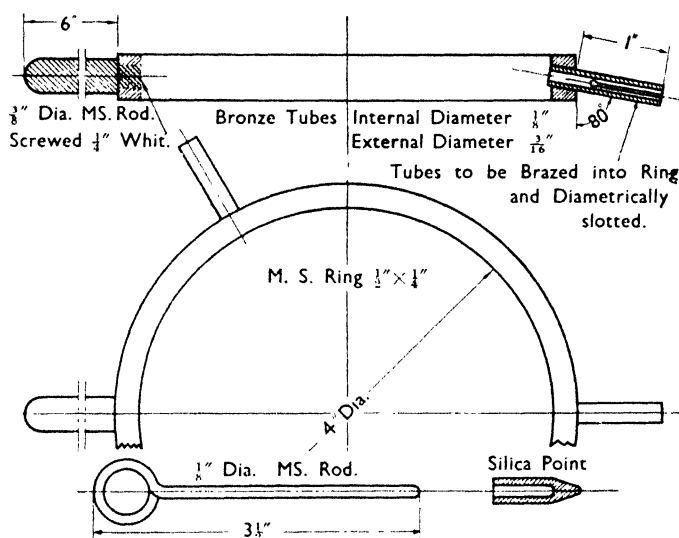
4. **Insoluble Matter (" Free-Carbon ").**—One or two innovations have been introduced in the 1938 edition of *Standard Methods* and these justify a brief outline of this test as applied to pitch.

Note.—The dimensions in the above figure are for guidance.

FIG. 74.—Volatile Matter in Pitch—Three-Arm Crucible Support with Silica Points.

1 g. of the sample, finely divided if possible, is mixed with 100 ml. of pure toluole at laboratory temperature. The particles of pitch are thoroughly broken up by means of a glass rod and, after twenty minutes' settlement, the supernatant liquid is filtered, either through filter paper or through a Gooch crucible prepared with asbestos. The residue in the beaker is treated in exactly the same way with a further 100 ml. of pure toluole at laboratory temperature and then with three successive quantities, each of 100 ml. of hot pure toluole in exactly the same manner, except that the beaker is stood on a water-bath during the settling periods and each settling period need only be five minutes.

The residue is transferred to the filter and the washing continued

[1] *Methods of Testing Coal Tar Products*, The Barrett Co., New York.

until a further 500 ml. of hot pure toluole has been used. Drying and weighing of the residue follow on the usual lines. Finally the residue is incinerated and the weight of ash-free free-carbon is calculated.

5. **Ash.**—1 g. of the sample is incinerated to constant weight in a platinum or porcelain crucible. If the volatile matter has been determined, the ash may conveniently be determined by incinerating, in the same crucible, the residue thereby obtained.

6. **Hardness and Breaking Point.**—The needle penetrometer employed in America for the examination of bituminous materials [1] may be used for the determination of the hardness of pitch. The Dow penetrometer, simplified in construction by Richardson and Forrest,[2] is the type of instrument in common use. Unless otherwise specified, penetration is defined as the consistency of a bituminous material expressed as the distance that a standard needle penetrates vertically a sample of the material under known conditions of loading, time and temperature. Where the conditions of the test are not specifically mentioned, the load, time and temperature are understood to be 100 g., 5 secs., 25° (77° F.) respectively, and the units of penetration to indicate hundredths of a centimetre.

The determination of the breaking point of a sample of pitch gives an indication of the ductility of the pitch at low temperatures. For asphaltic materials the most widely used apparatus is that of Dow and Smith.[3] The Barrett Company of America use the breaking point machine shown in Fig. 75. The brass mould, 12 in. long by 1 in. wide by $\frac{1}{4}$ in. deep, is filled with a slight excess of liquid pitch and allowed to cool. The excess of pitch above the top of the mould is then removed by means of a hot knife-blade, the pitch removed from the mould and cut into three pieces each 4 in. in length. One of these pieces is then placed vertically in the clamp of the breaking-point machine the operation of which is as follows :—

The apparatus consists essentially of the clamp A, which holds the test piece, and the pin C carried by the wheel D, which is turned by the handle E. The back of the clamp A is concentric with the wheel D and rounded to $\frac{3}{16}$th in. diameter. When in the operating position the pin C is on the same side of the test piece as the movable jaw of the clamp. The action of the machine is such that by turning the handle E the large wheel is caused to revolve counter-clockwise. The pin C is thus brought in contact with that portion of the test piece projecting above the clamp, and as its motion is continued, bends the test piece about the rounded back of clamp A. The handle E must

[1] D 5-25, *Amer. Soc. Testing Materials, Standards*, 1936, ii. 1080.

[2] *Proc. Amer. Soc. Testing Materials*, 1907, **7**, 626 ; *ibid.*, 1909, **9**, 600.

[3] *Munic. Eng.*, 1911, **40**, 437 ; D 113-35, *Amer. Soc. Testing Materials, Standards*, 1936, ii. 1058.

be turned at a rate of eight revolutions in ten seconds, which is equivalent to a 180 degrees bend in ten seconds. A suitable control

Brass Mould

Side View

Front View

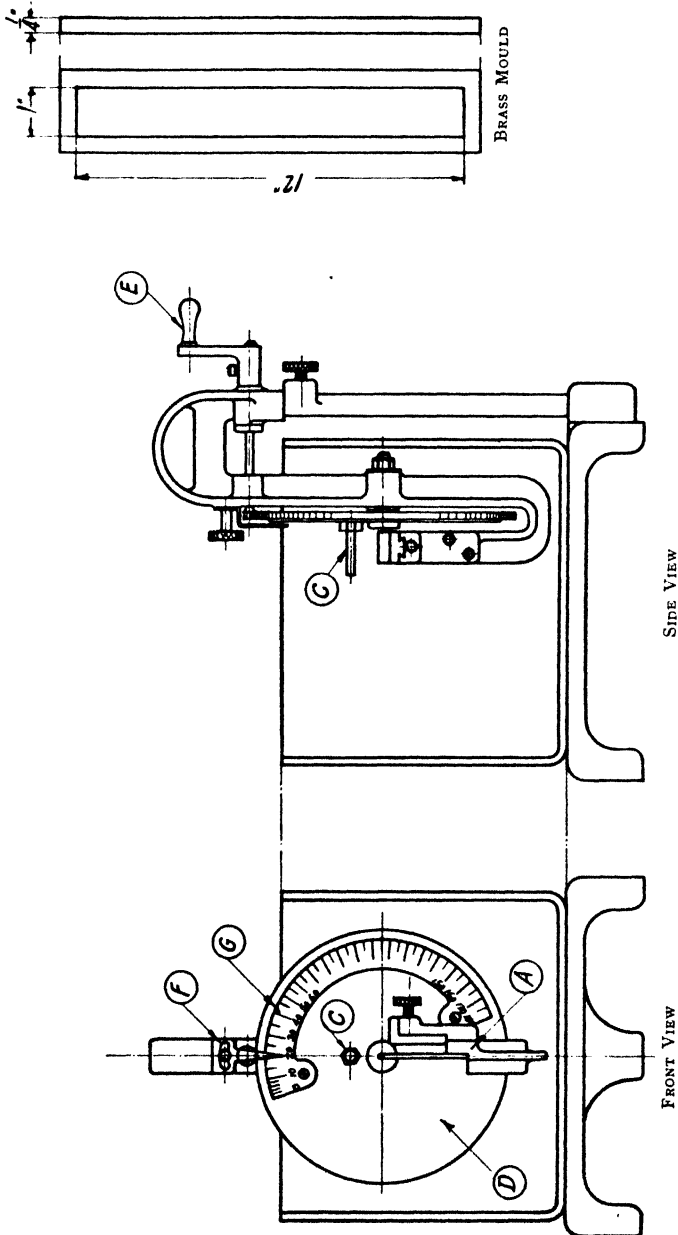



Fig. 75

is to set a metronome at ninety-six beats per minute and to turn the handle at the rate of a half revolution per beat.

Unless the piece breaks the bending is continued to the limit of

motion of the apparatus which, in effect, is a 180 degrees bend. When the test piece is at or below its breaking temperature it will break through. Temperature control is secured by immersing the specimens and the arm carrying the clamp and large wheel in a suitably-sized water-bath, the temperature of which is maintained constant for at least ten minutes before a test is made. Preliminary tests are made over a range of temperature calculated to approximate the breaking point, this range then being narrowed until a lowering of the temperature by one degree will cause a break to occur when the test at the one degree higher temperature shows no break. The temperature at which the break occurs under the above conditions is reported as the breaking point.

7. **Distinguishing Coal Tar Pitch of Different Origins.**—The distinction between coal tar pitch of different origins (gas tar, coke-oven tar, and blast-furnace tar) is easily ascertained by determining the free-carbon and the ash. Horizontal retort tar pitch is characterized by its high free-carbon content which is seldom less than 25 to 30 per cent. Blast-furnace pitch contains from 6·8 to 11·1 per cent. of ash, whilst pitch from gas tar or coke-oven tar scarcely ever yields more than 0·1 per cent.[1] If a coal tar pitch yields less than 1 per cent. of ash it is almost certainly not blast-furnace pitch. Blast-furnace pitch is of but little value for most purposes on account of its want of tenacity and elasticity. Coal tar pitch can readily be distinguished from other varieties, such as brown coal tar pitch, wood tar pitch, stearin or woolfat pitch, or from natural asphalt or oil asphalt, by heating the sample over a naked flame. The smell so obtained is quite characteristic for each variety. The behaviour with petroleum benzine may also be used; coal tar pitch is almost insoluble, whilst brown coal tar pitch is nearly completely soluble.[2] The solubilities of wood tar pitch and stearin pitch in the same solvent are given in the following table,[3] due to Davies :—

	In petroleum benzine.		Ash. Per cent.	Sulphur. Per cent.
	Soluble. Per cent.	Insoluble. Per cent.		
Wood tar pitch 1	24·44	75·56	0·20	0·69
„ „ „ 2	18·70	81·80	1·06	0·41
„ „ „ 3	15·86	84·14	0·48	0·59
Stearin pitch	71·05	28·95	5·50	0·04

[1] Buchanan, *J. Soc. Chem. Ind.*, 1894, **13**, 1098.

[2] Scheithauer, *Muspratt's Handbuch der technischen Chemie*, 4th ed., vol. vi., p. 1982.

[3] *Chem. and Drug.*, 1883, **25**, 504; *cf.* Donath and Margosches, *Chem. Ind.*, 1904, **27**, 220; Graefe, *Chem.-Ztg.*, 1906, **30**, 298.

Mansbridge [1] outlines a scheme for the examination and identification of pitch of unknown origin, according to which pitches may be separated into two classes by their behaviour when treated with alcoholic soda or potash solution. If the sample is wholly or partially saponified it may be bone pitch, wool-grease pitch, or a variety of stearine pitch; if saponification does not occur, the sample is a coal tar pitch, a mineral oil pitch, a natural asphalt, an ozokerite pitch, or a wood tar pitch. Further subdivision of these classes is indicated by the results of treatment of the sample with white spirit, and the sample identified finally by special tests. Thus coal tar pitches, including blast-furnace and coke-oven pitch, are insoluble in white spirit. These give a characteristic smell when heated, which serves to distinguish them from a few insoluble mineral oil pitches and insoluble wood tar pitch; the last-named gives a woody smell when heated, like Stockholm tar. The grade of white spirit recommended should have a boiling-point near to 140° and a sp. gr. between 0·785 and 0·800. The so-called diazo reaction is used for identifying bituminous materials containing phenols and including wood tar and wood tar pitch, shale tar, peat and lignite tars and pitches, bone tar pitch and the various coal tar pitches. Oil-gas and water-gas tars and pitches contain only a trace of phenols and give but a slight diazo reaction. The test as devised by Graefe [2] is carried out by boiling 2 g. of the sample to be examined with 20 ml. of normal aqueous sodium hydroxide for approximately five minutes. The liquid is cooled and filtered. If the filtrate is dark coloured it may be lightened by shaking with finely pulverized sodium chloride and again filtering. It is now cooled in ice and a few drops of diazobenzene chloride solution (freshly prepared by treating aniline with hydrochloric acid and sodium nitrite) added. If phenols are present, a more or less fugitive red coloration results, sometimes accompanied by a reddish precipitate. If the diazo reaction is obtained, the bituminous material may be a pitch or an asphalt "cut-back" with a high boiling-point distillate containing phenolic bodies and derived from coal tar or one of the above-named tars. To apply the test under these conditions, Marcusson [3] uses the following procedure:—

10 g. of the bituminous substance is dissolved in 15 ml. of benzole, and the solution poured into 200 ml. of 88° petroleum naphtha. The resulting precipitate is filtered, washed with petroleum naphtha and dried. It is then boiled under a reflux condenser for fifteen minutes with $N/2$ alcoholic potassium hydroxide to extract the phenols, the liquid cooled and filtered, the alcohol evaporated and the residue

[1] *J. Soc. Chem. Ind.*, 1918, **37**, 182 T.
[2] *Chem.-Ztg.*, 1906, **30**, 298; *cf.* Marcusson and Eickmann, *Chem.-Ztg.*, 1908, **32**, 965.
[3] *Chem. Rev. Fett-Ind.*, 1911, **18**, 47; *Mitt. Materialprüf.*, 1920, **38**, 79.

dissolved in water. The liquid is clarified with sodium chloride, filtered, and the filtrate used for the diazo reaction test as above.

If a straight distilled pitch containing phenols is present a positive reaction is obtained. If the original substance gives the diazo test, but the residue treated as above does not, then the substance is a mixture of high-boiling oils containing phenols with a substance such as an asphalt, free from phenols. If the bituminous substance contains calcium carbonate the phenolic bodies present combine with the lime to form insoluble calcium phenolate, which gives only a faint diazo reaction. If such a substance be treated with a solvent in the presence of hydrochloric acid, the calcium phenolate is decomposed and the reaction becomes much more delicate.

Loebell [1] states that viscous bituminous substances are frequently little attacked by boiling for a short period with sodium hydroxide solution. Accordingly, he recommends that 2 g. of the material to be tested be warmed in a porcelain dish on the water bath mixed with the same quantity of sand and, after cooling, well shaken in a wide test-tube with acetone. If the solution remains colourless or is only very faintly yellow in colour, coal tar pitch is not present. If a deep-coloured solution results, it is filtered, the acetone removed completely by evaporation and the brownish-red oily residue treated as described by Graefe. With easily pulverizable materials admixture with sand may be omitted. According to Nellensteyn and Sauerbier [2] the diazo test is unreliable in the presence of colophony, but good results are obtained using Millon's reagent. 10 g. of the bituminous material is boiled for twenty minutes with 25 ml. of normal sodium hydroxide solution, the solution filtered and rendered faintly acid with nitric acid. It is then concentrated to 5 to 10 ml., 5 ml. of Millon's reagent added, and the mixture heated in a test-tube in boiling water for thirty minutes. If coal tar pitch is present in amount exceeding 1 per cent. a coloration will develop. According to Marcusson,[3] the behaviour of the substance towards sulphuric acid provides a means of distinguishing coal tar pitch from natural asphalts. 3 g. of the carbon disulphide, chloroform or benzole-soluble portion of the substance, after evaporation of the solvent, is treated with 6 ml. of 95 per cent. sulphuric acid in a stout test-tube heated in a boiling water-bath for forty-five minutes and continuously agitated. The contents of the test-tube are then poured into 500 ml. of cold water. Coal tar pitch and wood tar pitch dissolve completely to a deep black solution, and upon filtering leave little or no residue. Natural asphalts as well as petroleum residues, asphaltites and lignite tar pitch produce a copious insoluble precipitate. The solution is allowed to stand for one hour, and the liquid decanted

[1] *Chem.-Ztg.*, 1911, 35, 408. [2] *Z. angew. Chem.*, 1929, 42, 722.
[3] *Die Natürlichen und Künstlichen Asphalte*, Leipzig, 1921, pp. 91 and 106.

carefully through a weighed and prepared Gooch crucible of about 7 cm. diameter. The residue is washed with water and finally transferred to the filter. Washing is then continued until the washings are no longer acid to methyl orange, the residue is dried at 105° and weighed.

The sulphur content of a sample of bituminous material is indicative of its origin. In general, natural asphalts contain from about 2 to 12 per cent., brown coal tar pitch up to 2 per cent., Galician oil residues not generally over 1 per cent., and coal tar pitch between 0·6 and 0·8 per cent. Mexican asphaltic-base oil residues contain up to 6 per cent. The dimethyl sulphate test has also been proposed as a qualitative test for detecting mixtures of pitches with asphalts. It is based upon the fact that unsaturated hydrocarbons are soluble in dimethyl sulphate (or diethyl sulphate [1]), whereas saturated hydrocarbons are not. The material to be tested is distilled and 4 ml. of the distillate is shaken with 6 ml. of dimethyl sulphate in a 10 ml. cylinder graduated to 0·1 ml. After standing, the percentage of insoluble saturated hydrocarbons is noted.[2] Solid paraffins are absent from pitches and tars from high-temperature processes; solid paraffins are more or less present in non-asphaltic and semi-asphaltic petroleum, are rarely found in natural asphalts, and only in traces in asphalts produced from strictly asphalt-base petroleums.

Finally, the detection of anthracene in tar products by means of the anthraquinone reaction is valuable for purposes of identification. The sample under examination is distilled and the 270° to 355° fraction collected. To 5 g. of this fraction, weighed whilst hot in order to obtain a uniform sample, is added, after cooling, 10 ml. of absolute alcohol. The solids are allowed to crystallize, the liquid decanted and the dried solid substances examined for anthracene by the method described on p. 304.

[1] Taylor, *Ind. Eng. Chem.*, 1927, **19**, 76.

[2] Sommer, *Ind. Eng. Chem.*, 1910, **2**, 181; Reeve and Lewis, *ibid.*, 1913, **5**, 293; *Mitt. Materialprüf.*, 1925, **42**, 67.

APPENDIX

1. Apparatus for Standard Methods

In the immediately following sections the general form of the specialized apparatus prescribed in *Standard Methods* has been summarized; the original text should be consulted for the full particulars required for manufacturing purposes or for checking compliance with the specifications.

(a) *Thermometers*

In basic design, quality of material, etc., these are closely in line with the British Standard series of General Purpose Laboratory Thermometers [1] and, in the two cases where it is possible, the thermometers from that series have been accepted for use in the relevant tests on tar products. As regards range, extent of subdivision of the range and consequential dimensional requirements, the thermometers for standard tar testing are characteristic; the more interesting details are shown in the following table.

Selected Details of Standard S.T.P.T.C. Thermometers

Range.	Immersion.	Maximum error.	Maximum distance from bottom of bulb to top of contraction chamber.	Limit of accuracy of N.P.L. test.
	mm.	degree.	mm.	degree.
−10° to 20° C.	100	±0·2	(a)	±0·05
0° ,, 120° C.	100	±0·8	(a)	±0·1
0° ,, 120° C.	Total	±0·3	(a)	±0·1
90° ,, 400° C.	100	±4·0	25	±0·5
15° ,, 45° C.	100	±0·4	(a)	±0·05
65° ,, 90° C.	100	±0·4	25	±0·05
70° ,, 130° C.	100	±0·6	25	±0·1
50° ,, 210° C.	100	±0·8	25	±0·1
105° ,, 115° C.	100	±0·4	25	±0·05
130° ,, 160° C.	100	±0·6	25	±0·05
150° ,, 250° C.	100	±1·2	25	±0·2
40° ,, 85° F.	100	±0·4	(a)	±0·1
175° ,, 230° C.	100	±1·2	25	±0·2
39·5° ,, 70·5° C.	100	±0·4	25	±0·05

Notes.—

(*a*) These thermometers do not require a contraction chamber, but if there be any enlargement of the bore below the scale, it shall be placed entirely within a distance of 25 mm. from the bottom of the bulb.

(*b*) The corrections to be applied shall not change between successive test points by more than five times the figure in the last column, which shows the limit of accuracy of the test which the National Physical Laboratory will apply to each thermometer submitted for test.

(*c*) The requirements for the first and last thermometers are such that the British Standard thermometers A20C/100 and A70C/100 of B.S. 593—1935: General Purposes Laboratory Thermometers, may be used for all tests for which the first and last thermometers in the table are respectively prescribed.

[1] *British Standards Institution, B.S.* 593, 1935 (shortly to be re-issued in revised form).

(b) *Hydrometers*

For determinations of density, the British Standard series of density hydrometers [1] is prescribed in *Standard Methods*; the British Standard series is, however, a "general purposes" series and the hydrometers indicated in the following table represent those more particularly suitable for testing tar and its products.

British Standard Density Hydrometers Available for Use with Tar and Tar Products

Series.	Density equivalent of one subdivision. g./ml.	Maximum permissible scale error. g./ml.	Range of individual hydrometers in series covering range of density 0·650 to 1·300 g./ml. of tar and tar products.	Number of hydrometers for range 0·650 to 1·300 g./ml.
0·0005 × 100	0·0005	±0·0004	0·650 to 0·700 g./ml.; 0·700 to 0·750 g./ml. and so on up to and including 1·250 to 1·300 g./ml.	13
0·001 × 100	0·001	±0·001	0·600 to 0·700 g./ml.; 0·700 to 0·800 g./ml. and so on up to and including 1·200 to 1·300 g./ml.	7
0·002 × 100	0·002	±0·002	0·600 to 0·800 g./ml.; 0·800 to 1·000 g./ml. and so on up to and including 1·200 to 1·400 g./ml.	4
0·0005 × 50	0·0005	±0·0004	0·650 to 0·675 g./ml.; 0·675 to 0·700 g./ml. and so on up to and including 1·275 to 1·300 g./ml.	26
0·001 × 50	0·001	±0·001	0·650 to 0·700 g./ml.; 0·700 to 0·750 g./ml. and so on up to and including 1·250 to 1·300 g./ml.	13
0·002 × 50	0·002	±0·002	0·600 to 0·700 g./ml.; 0·700 to 0·800 g./ml. and so on up to and including 1·200 to 1·300 g./ml.	7
0·001 × 25	0·001	±0·001	0·650 to 0·675 g./ml.; 0·675 to 0·700 g./ml. and so on up to and including 1·275 to 1·300 g./ml.	26
0·002 × 25	0·002	±0·002	0·650 to 0·700 g./ml.; 0·700 to 0·750 g./ml. and so on up to and including 1·250 to 1·300 g./ml.	13

In connection with sp. gr. determinations, there is no British Standards Institution series of hydrometers; the general form of the sp. gr. hydrometers for Standard Methods is indicated by the particulars in the following table. The series is almost identical with that of the Institute of Petroleum,[2] the principal difference being nominal for most practical purposes, viz. that the petroleum series is graduation for recording $S_{60° F./60° F.}$ while the tar series is graduated for recording $S_{15·5° C./15·5° C.}$

S.T.P.T.C. Specific Gravity Hydrometers

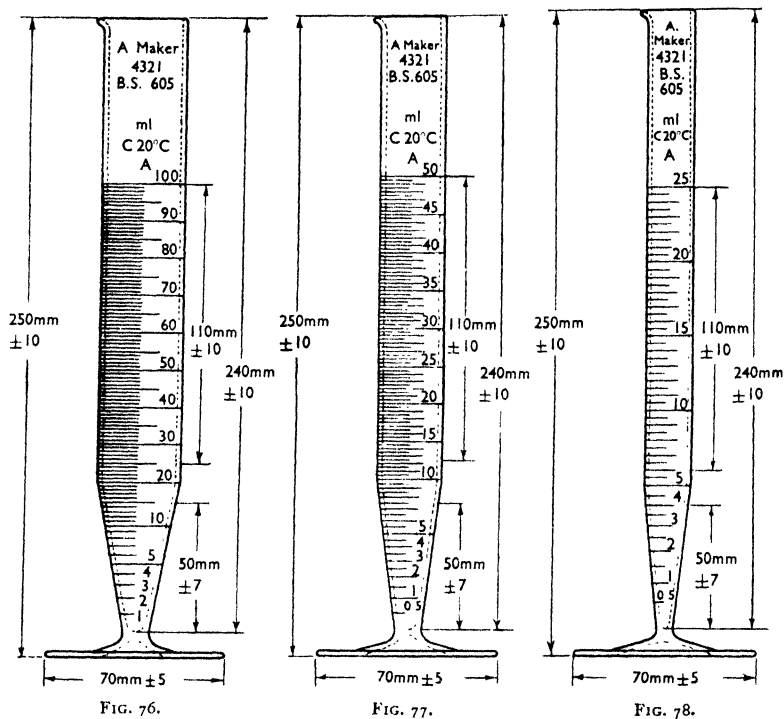
	Series A.	Series B.	Series C.	Series D.
Maximum overall length	360 mm.	250 mm.	195 mm.	150 mm.
Maximum diameter of the bulb	40 ,,	30 ,,	25 ,,	20 ,,
Length of the nominal range corresponding to 0·05 change in specific gravity — not less than	155 ,,	75 ,,	50 ,,	35 ,,
Length of the nominal range corresponding to 0·05 change in specific gravity — not more than	175 ,,	90 ,,	60 ,,	40 ,,
Number of subdivisions in nominal range	100	50	25	25
Tolerance of accuracy	±0·0004	±0·0010	±0·0015	±0·0020

[1] Extracted by permission from *B.S.* 718, 1936 (price 3s. 6d.).

[2] *Standard Methods for Testing Petroleum and its Products*, 1935, p. 144.

(c) *Crow Receivers*

These are the British Standard series,[1] and it is sufficient to refer to Figs. 76 to 78 and the table below for the general design, etc., of these vessels.

FIG. 76. FIG. 77. FIG. 78.

100 ml., 50 ml., and 25 ml. Crow Receivers.

Tolerance on Capacity of British Standard Crow Receivers

Class of tolerance.	100 ml. receiver.		50 ml. receiver.		25 ml. receiver.	
	Up to and including 10 ml. mark.	Above 10 ml. mark.	Up to and including 5 ml. mark.	Above 5 ml. mark.	Up to and including 2·5 ml. mark.	Above 2·5 ml. mark.
	ml.	ml.	ml.	ml.	ml.	ml.
Class A tolerance	±0·2	±0·4	±0·1	±0·2	±0·04	±0·1
Class B tolerance	±0·4	±0·8	±0·2	±0·4	±0·1	±0·2

(d) *Separating Funnel Receivers*

These, used for instance in the determination of neutral oils in carbolic and cresylic acids, are shown in Figs. 79 and 80. The amount of separated material, the volume of which is to be measured, determines which of the two alternatives is used in any particular test.

[1] Extracted by permission from *B.S.* 605, 1935.

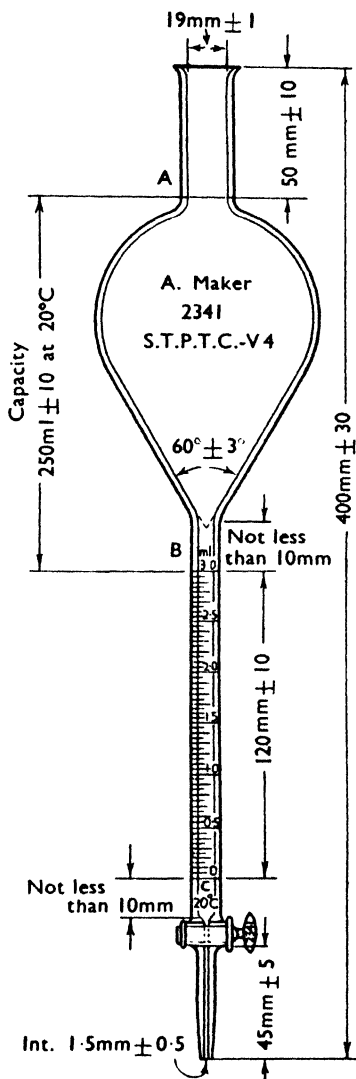



FIG. 79.—Separating Funnel Receiver.

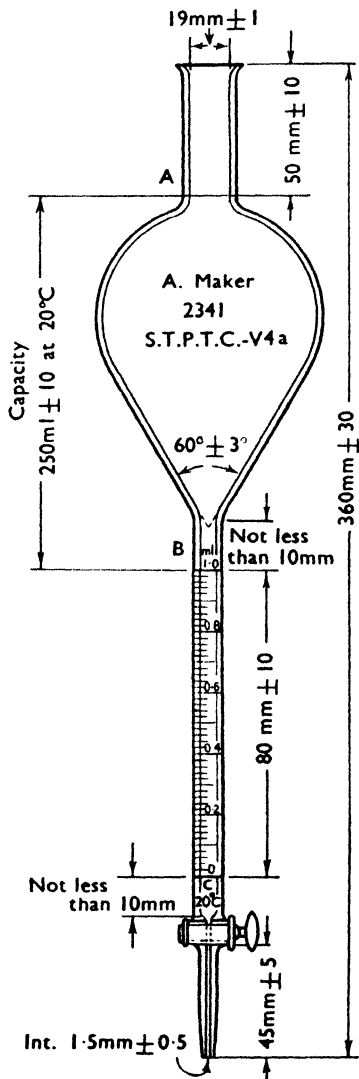



FIG. 80.—Separating Funnel Receiver.

The tolerances on capacity are given below :—

	Funnel with 3 ml. scale.	Funnel with 1 ml. scale.
	ml.	ml.
Class A . .	±0·03	±0·01
Class B . .	±0·05	±0·02

(c) *Phenols Flasks*

Standard Methods requires two phenols flasks, for alternative use according as the amount of separated phenols is greater or less than 10 ml. ; the flasks are two

of the three covered by the British Standard series of Flasks with Graduated Necks [1]; the relevant flasks are shown in Figs. 81 and 82, and the tolerances on capacity are given below.

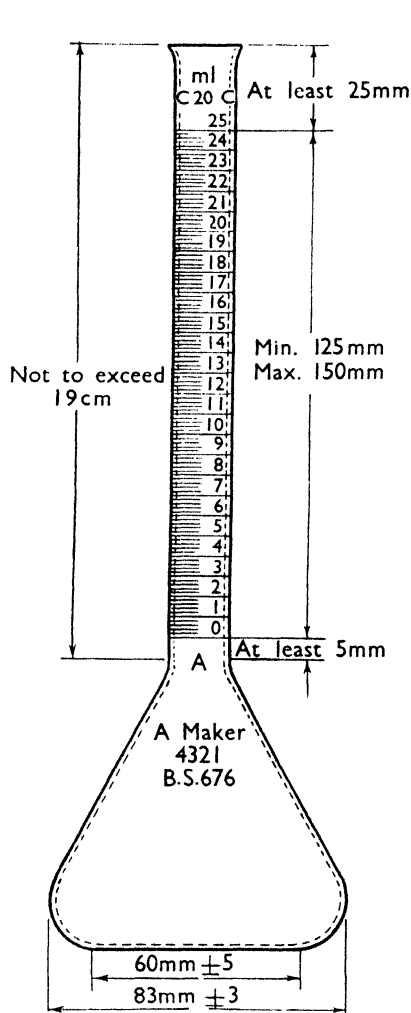



FIG. 81.—Large Phenols Flask.

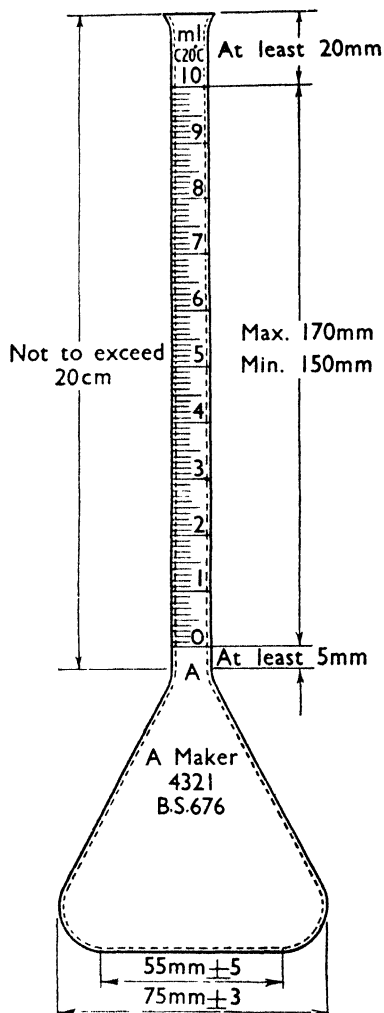



FIG. 82.—Small Phenols Flask.

	200 ml. flask with 25 ml. scale.		150 ml. flask with 10 ml. scale.	
	Class A.	Class B.	Class A.	Class B.
	ml.	ml.	ml.	ml.
Maximum permissible error on capacity corresponding to any graduation mark	±0·1	±0·2	±0·04	±0·08
Maximum permissible difference between the errors at any two graduation marks	0·1	0·2	0·04	0·08

[1] Extracted by permission from *B.S.* 676, 1936.

(f) *Dean and Stark Apparatus*

The relevant British Standards [1] are in course of revision and, pending the appearance of the revised provisions, *Standard Methods* specifies the forms which, with possibly minor modifications, will ultimately appear as the British Standards. The general design is illustrated in Figs. 83 to 89, but the units to the new British

FIG. 84.—Condenser.

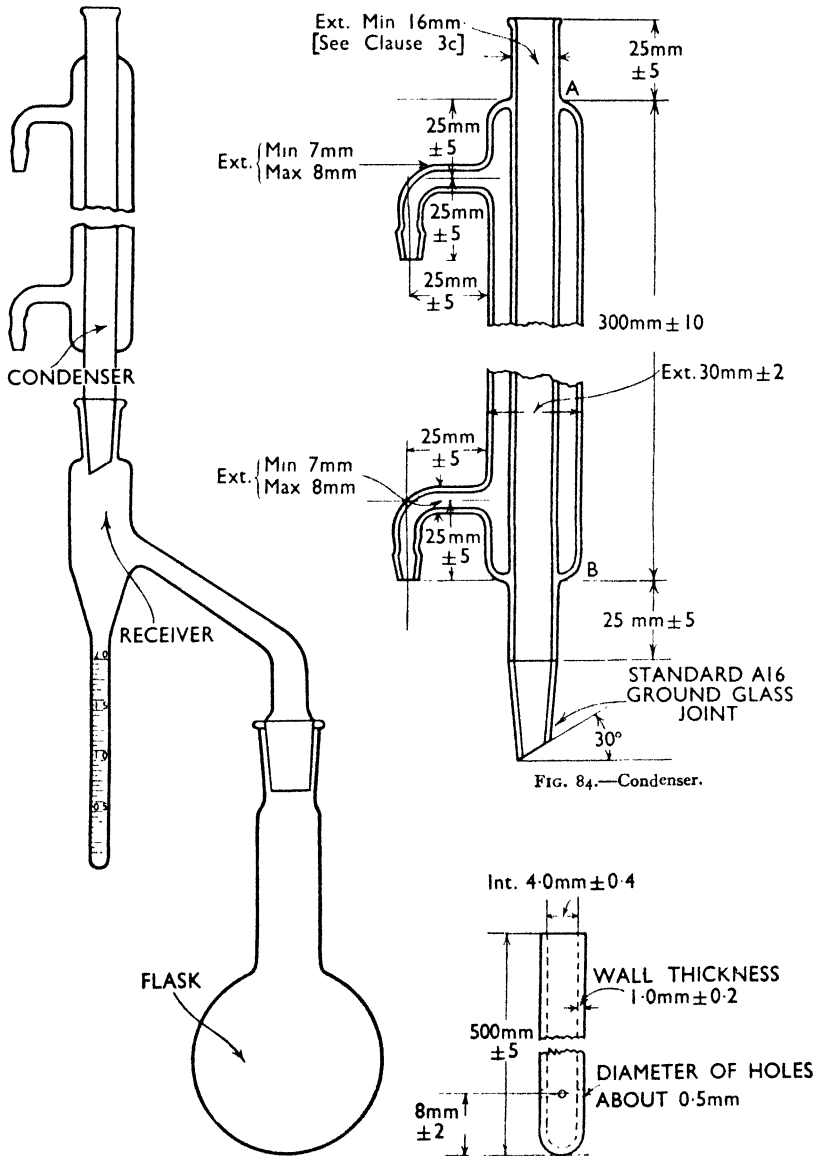



FIG. 83.—Assembly with 2 ml. Receiver.

FIG. 85.—Spray Tube.

Dean and Stark Apparatus.

[1] *British Standards Institution*, *B.S.* 756, 1939.

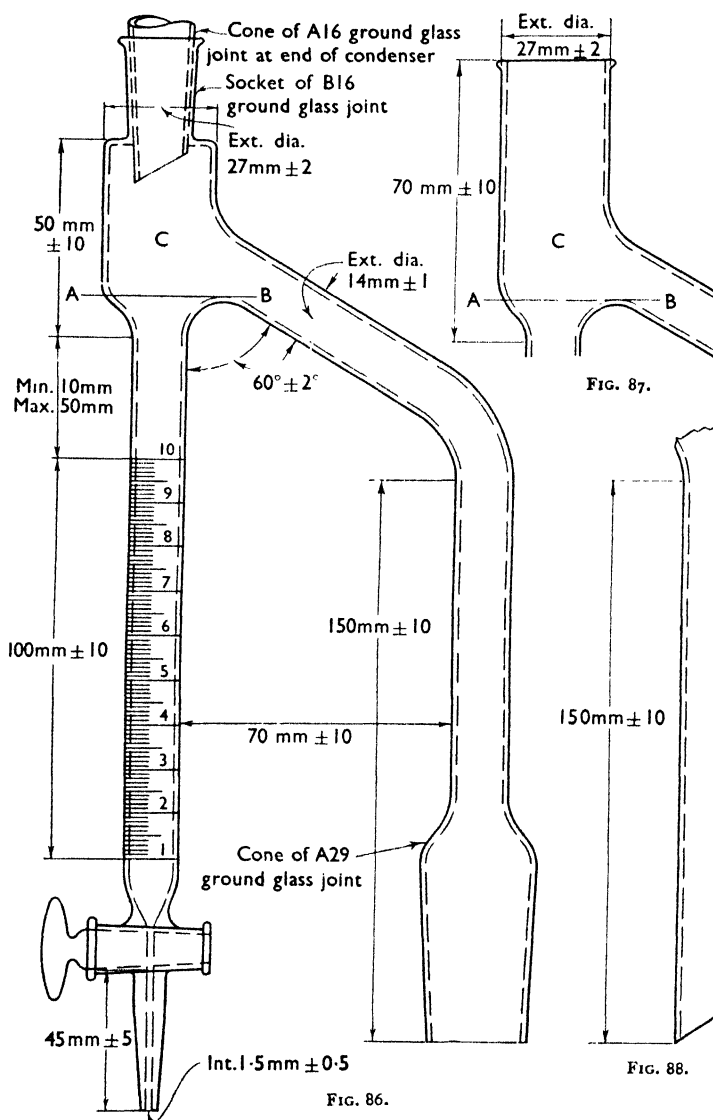



Fig. 86.

Fig. 87.

Fig. 88.

Inscriptions appear on Receiver as required by specification.

Fig. 86.—10 ml. Receiver with Ground Glass Joints.
Fig. 87.—Design of Upper Chamber without Ground Glass Socket.
Fig. 88.—Design of Side Tube without Ground Glass Cone.

Dean and Stark Apparatus.

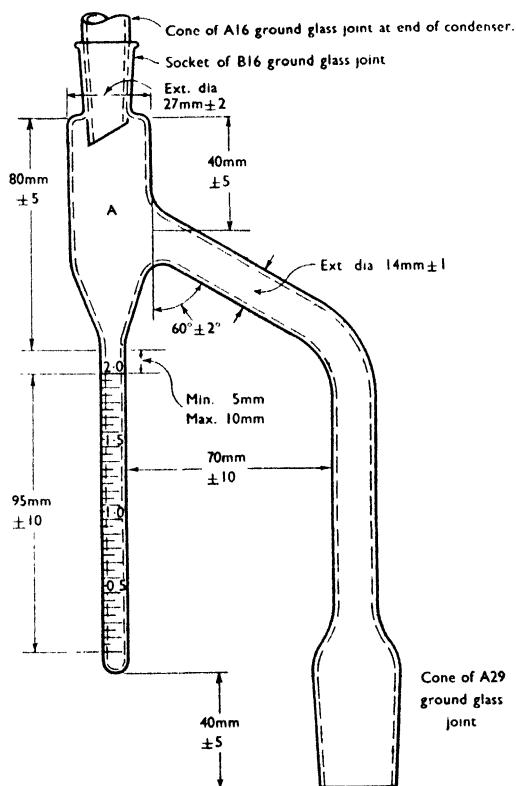
Standard will automatically become the standards for tar tests when the revision of the former is complete. This does not, however, apply to the boiling flask, which must be as prescribed in the relevant Standard Method. The spray tube shown in Fig. 85 is used at the end of the distillation process to wash down, by means of solvent, any drops of water which adhere to the lower end of the inner condenser tube.

Inscriptions appear on apparatus as required by specification.

FIG. 89.—Dean and Stark Apparatus—2 ml. Receiver.

The tolerance on capacity of the 10 ml. receiver is ±0·06 ml. at any point on the scale and the difference between the errors at any two points must not exceed 0·06 ml.; in the case of the 2 ml. receiver, the figure is 0·03 ml. These are Class A tolerances and no Class B tolerances are admitted.

(g) *Sulphonation Apparatus*

Again, two units are provided for alternative use according to the amount of unsulphonated material to be measured. The units are illustrated in Figs. 90 and 91, and the tolerances on capacity are given below.

	Sulphonation apparatus with 10 ml. scale.	Sulphonation apparatus with 2 ml. scale.
	ml.	ml.
Class A . .	±0·06	±0·02
Class B . .	±0·10	±0·04

Inscriptions appear on apparatus as required by specification.

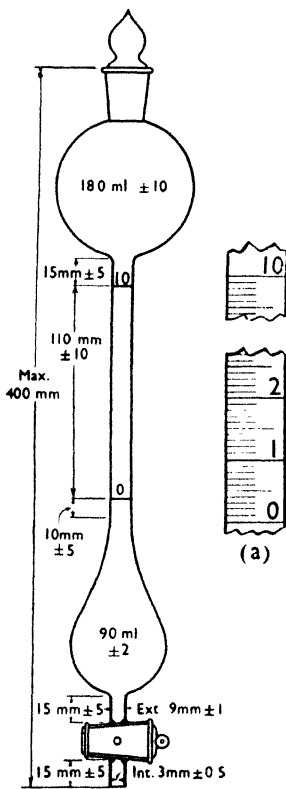



FIG. 90.—Sulphonation Apparatus. (Inset (*a*): Details of Graduation Markings.)

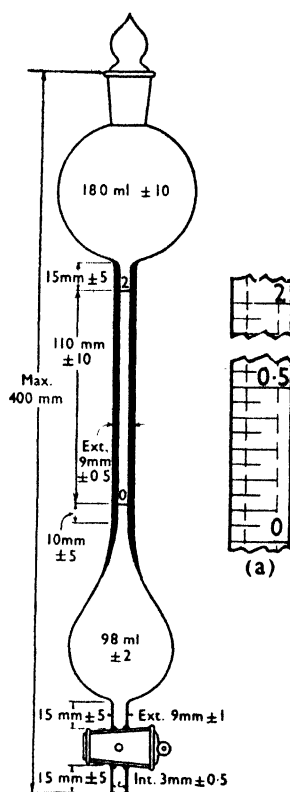



FIG. 91.—Sulphonation Apparatus. (Inset (*a*): Details of Graduation Markings.)

(h) *Phenols Separating Apparatus*

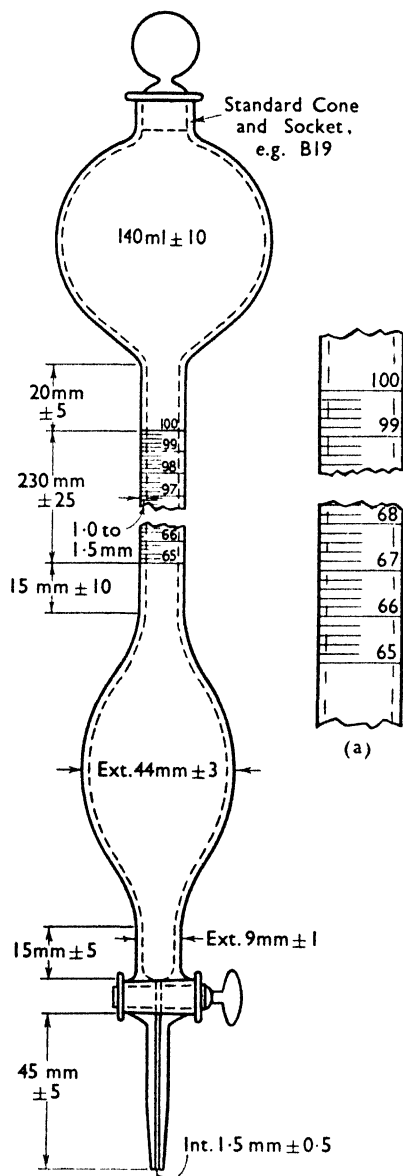
This is, apart from a little improvement in design, the apparatus recommended by the Barrett Co.; it is shown in Fig. 92 and the Class A and Class B tolerances are ±0·1 ml. and ±0·2 ml. respectively.

Inscriptions appear on apparatus as required by specification.

FIG. 92.—Phenols Separating Apparatus
(Inset (*a*) : Details of Graduation Markings.)

(i) *Nessler Cylinders*

These are the British Standard units[1] and are illustrated in Fig. 93 and the maximum permissible errors in capacity are ±0·8 ml. at both the 50 ml. and

[1] Extracted by permission from *B.S.* 612, 1935.

100 ml. marks on the 100 ml. cylinder and ±0·4 ml. at the mark on the 50 ml. cylinder.

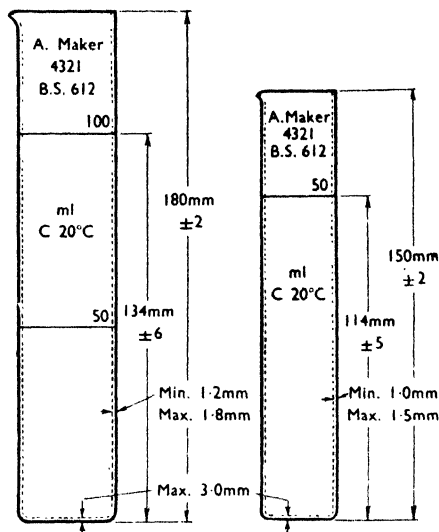



FIG. 93 —Nessler Cylinders.

(j) *Density Bottles*

Standard Methods recommends the use of the British Standard bottles [1] which are typified by the particulars in the table below; the 50 ml. size is shown, as an example of the series, in Fig. 94.

Certain Dimensions and Tolerances on Capacities of British Standard Density Bottles

	Nominal capacity of bottle.			
	10 ml.	25 ml.	50 ml.	100 ml.
Internal diameter in plane of top of neck * (mm.)	7·5	7·5	10·0	12·5
Length of engagement between stopper and neck * (mm.)	12	12	15	16
Taper of ground portion *	1 : 10 on diameter, corresponding to a semi-cone angle of 2° 51′ 45″ on the stopper			
Maximum permissible error on nominal capacity (±ml.)	0·004	0·006	0·008	0·012
Diameter of capillary through stopper :—				
Minimum (mm.)	0·5	0·5	0·5	0·5
Maximum (mm.)	1·0	1·0	1·5	1·5

* The dimensions quoted above are the same as the corresponding dimensions of the ground joints Nos. C7, C10 and C12 respectively of *B.S.* 572, 1934 : Interchangeable Conical Ground Glass Joints.

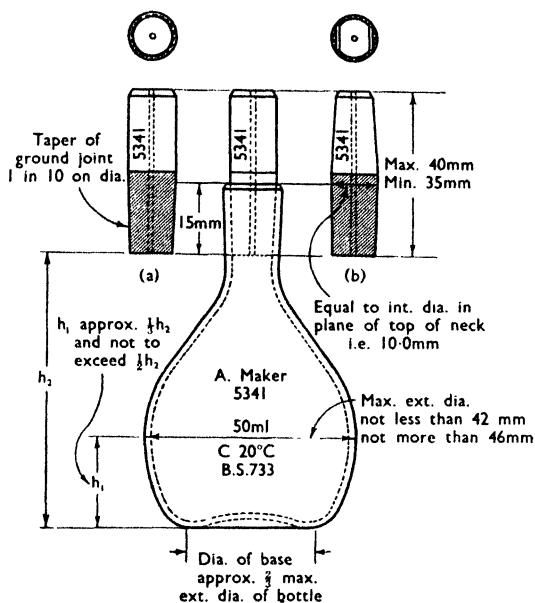
[1] Extracted by permission from *B.S.* 733, 1937.

The figure illustrates the specified dimensions of the bottle and of the alternative stoppers, but the profile of the bottle is approximate only and not intended as a precise drawing.

FIG. 94.—Density Bottles.

(k) *Distillation Flasks*

These again are the British Standard series [1] which, as is the case with the British Standards for apparatus used in testing tar and tar products, were adopted by the British Standards Institution from the 1929 edition of *Standard Methods.*

An alteration in the lengths of the side arms of the larger flasks in the British Standard series represents no obvious general advantage and is a disadvantage in connection with the testing of certain tar products for which specifications were developed on the basis of the 1929 flasks; the original dimensions are therefore retained in *Standard Methods* as indicated in the table (p. 448). That table is to be read in conjunction with Fig. 95, which additionally illustrates the positioning of the standard thermometers as is uniformly required in those Standard Methods which use the standard thermometers and flasks in conjunction.

[1] Extracted by permission from *B.S.* 571, 1934.

[TABLE.

Capacities and Dimensions of the British Standard Distillation Flasks with Details of Changes in Lengths of Side Tubes required by Standard Methods.

Distillation capacity *	V ml.	50	100	130	150	250	350	500	750	1000
Capacity of bulb Tolerance	V^1 ml. ...	65 ±3	130 ±5	170 ±6	195 ±7	325 ±10	455 ±12	650 ±15	975 ±20	1300 ±25
Internal diameter of neck between side arm and bulb Tolerance	D mm. mm.	16 ±1	16 ±1	18 ±1	18 ±1	20 ±1	22 ±1	24 ±1	28 ±1	30 ±1
Internal diameter of side tube Tolerance	D_1 mm. mm.	4 ±0·5	4 ±0·5	5 ±0·5	5 ±0·5	6 ±0·5	6·5 ±0·5	7·5 ±0·5	8·5 ±0·5	9·5 ±0·5
External diameter of side tube Tolerance	D_2 mm. mm.	6 ±0·5	6 ±0·5	7 ±0·5	7 ±0·5	8 ±0·5	9 ±0·5	10 ±0·5	11 ±0·5	12 ±0·5
Length of side tube † . Tolerance — S.T.P.T.C.	L mm. mm.	100 ±3	100 ±3	120 ±4	120 ±4	*124±4*	*140±4*	*140±4*	*160±5*	*160±5*
Length of side tube † . Tolerance — *B.S.* 571						160±5	180±5	200±5	210±6	220±6
Radius of curvature at base of neck ‡	r mm.	10	10	10	10	10	12	12	12	12
Thickness of walls of bulb, neck and side tube	mm.	0·8 to 1·2					1·0 to 1·5			

Notes.—

* The distillation capacity is the maximum volume of liquid which the bulb of the flask can satisfactorily accommodate for distillation.

† *For use in the standard tests it is necessary that the five largest British Standard distillation flasks in the above table should have the lengths of side arms shown in italics type.*

‡ It is desirable that the radius of curvature at the base of the neck should not be too small and so make a sharp angle between the neck and the bulb; on the other hand, the radius should not be so large as to make the bulb appreciably "pear-shaped." The radii given are for the guidance of manufacturers, but no rigid tolerances have been fixed.

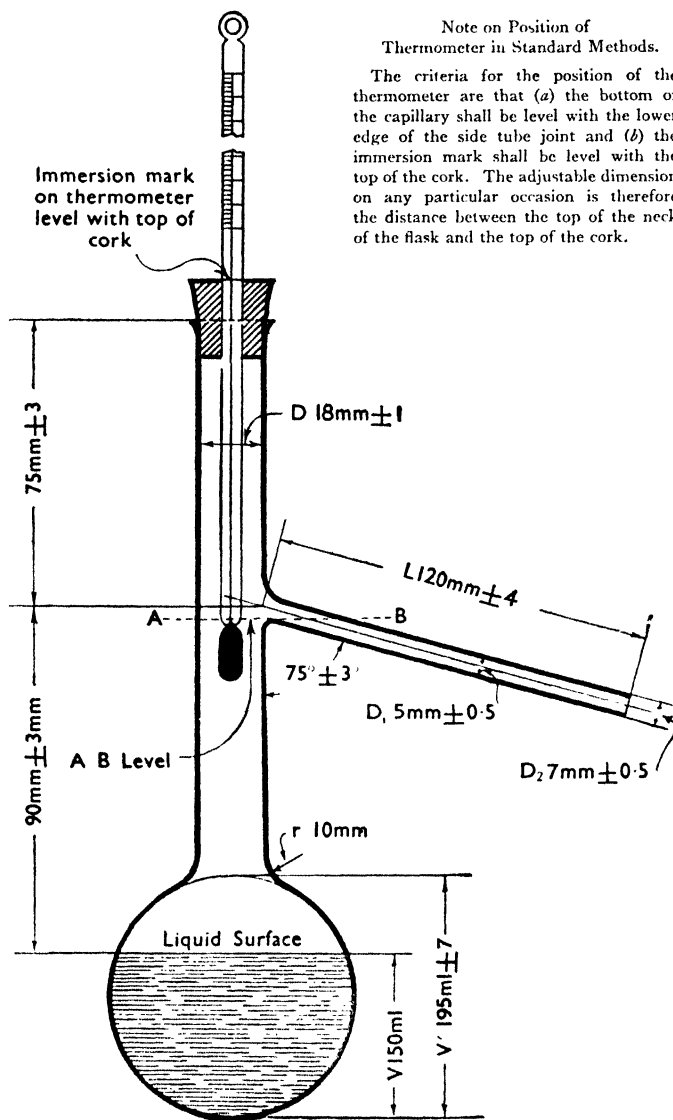



FIG. 95.—Distillation Flask of 100 ml. Distillation Capacity, with 100 mm. Immersion Thermometer in position as required by *Standard Methods*.

(1) *Boiling-point Flask*

This unit, illustrated in Fig. 96, is used in the determination of xylene in certain refined lower boiling products (see p. 254).

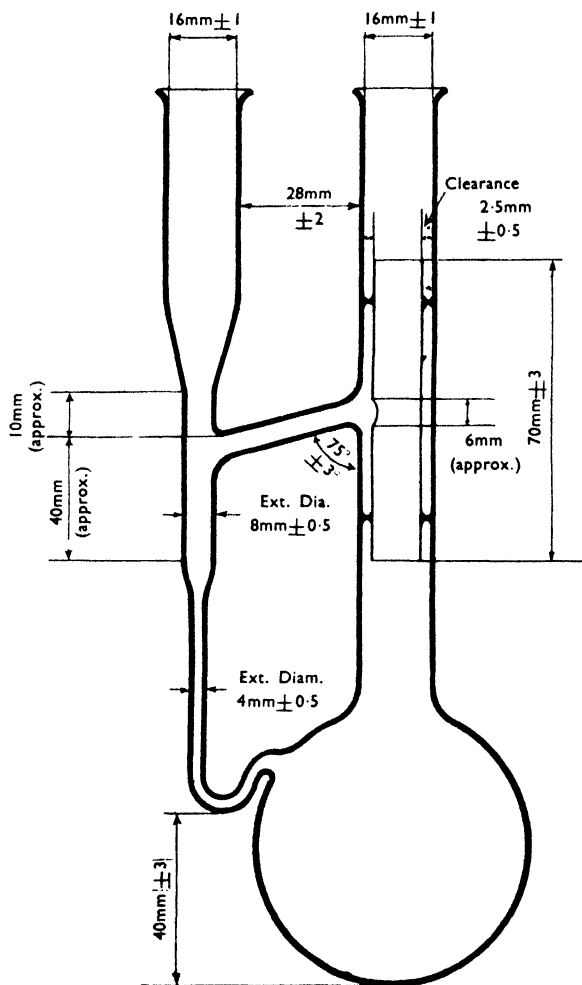



FIG. 96.—Boiling-point Flask.

(m) *Standard Condensers*

There are three standard condensers required in *Standard Methods*, and all are standardized in the British Standard for Distillation Apparatus.[1] First, there is an air condenser, consisting of a 600 mm. glass tube having an internal diameter of 20 mm. and a wall thickness of 1·0 to 1·5 mm. One end of the tube is finished square with the axis and the other is ground at an angle of about 45° thereto.

The other two condensers are of the Liebig form, made in glass, with the outer jacket fixed to the inner tube by means of rubber tubing; they are identical except in respect of their exit ends which are straight and turned respectively. These condensers are illustrated in Figs. 97 and 98.

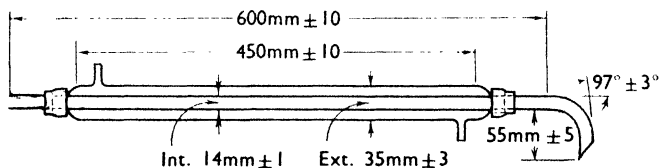



FIG. 97.—Liebig Condenser with Bent End.

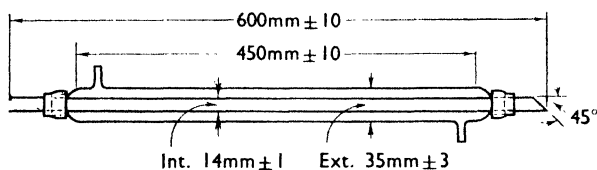



FIG. 98.—Straight Liebig Condenser.

(n) *Standard Fractionating Columns*

An attempt has been made in the 1938 edition of *Standard Methods* to devise standard designs for two pear columns in order that there may be at least no apparent cause for dispute, on the grounds of significant dissimilarity, in tests involving the use of these columns. Manufacturers now produce columns to remarkably close specifications having regard to the fact that the bulbs have to be blown individually and by hand. The designs shown in Figs. 99 and 100 for 8- and 12-bulb columns respectively should be found of more general applicability than in the testing of the tar products for which they were specifically developed. Figs. 101 and 102 show the details of the bulbs in the standard columns.

[1] Extracted by permission from *B.S.* 658, 1936.

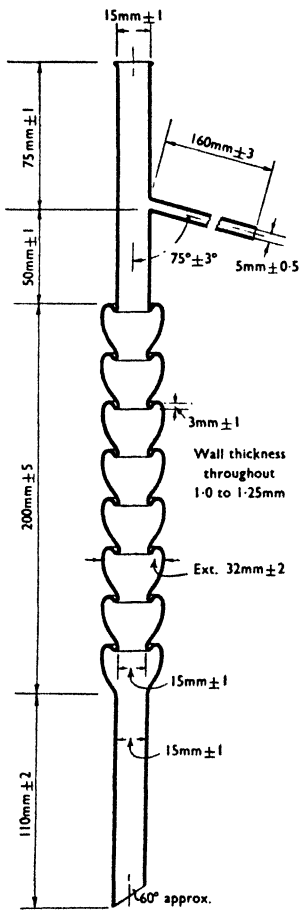



FIG. 99.—8-Bulb Fractionating Column.

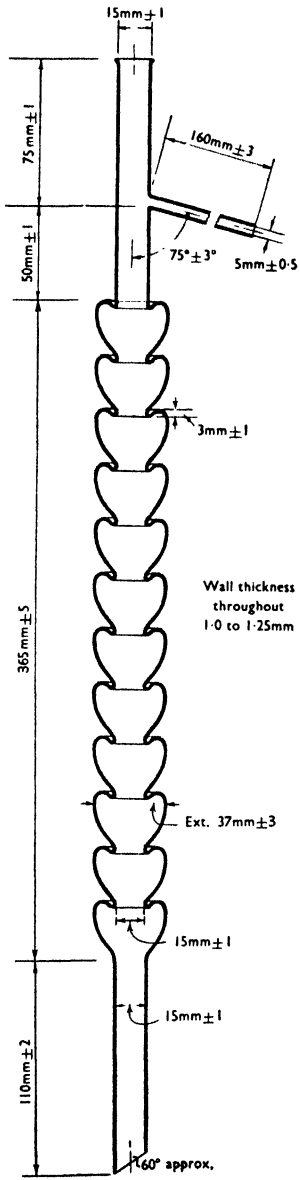



FIG. 100.—12-Bulb Fractionating Column.

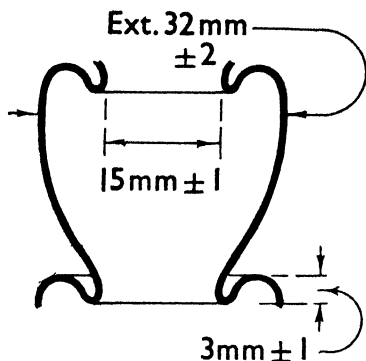
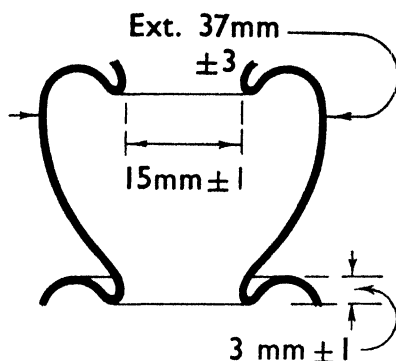



FIG. 101.—Bulb of 8-bulb Fractionating Column. FIG. 102.—Bulb of 12-bulb Fractionating Column.

(o) *Draught Screens*

There are three standard draught screens required in the Standard Methods for testing tar and its products. The first is simply a semicylindrical screen, 300 mm. in diameter and of a height appropriate for the test for which it is used. It is the most convenient form of screen for protecting the complete apparatus assembly from general draughts, in such tests as those for the softening of pitch; it is also convenient for protecting the flask, etc., in comparatively rough or preliminary distillations.

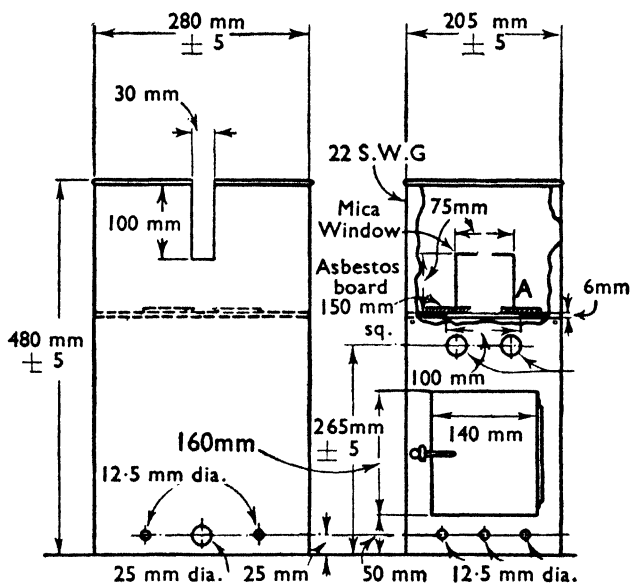



FIG. 103.—Rectangular Draught Screen.

A cylindrical screen, having a diameter of 300 mm., and conveniently formed in two parts hinged together, is required chiefly in fractionations involving the use of one of the standard pear columns. The height is determined largely by the column (8 or 12 bulb) used.

Finally, for straight distillations, the British Standard draught screen[1] is prescribed. It is shown in Fig. 103; in the principal standard form, the flask rests

[1] Reproduced by permission from *B.S.* 658, 1936.

Physical Constants of the More Common Constituents of Coal Tar

M = Molecular weight.
ρ_{20} = Density at 20° C., in g./ml.
α = Coefficient of cubical expansion, per Centigrade degree.
m.p. = Melting-point, degrees Centigrade.
c.p. = Crystallizing point, degrees Centigrade.
b.p. = Boiling-point at 760 mm., degrees Centigrade.
C.V. = Gross calorific value, in g. cal./g.

No.	Constituent.	Formula.	M.	ρ_{20}.	α.
1	Anthracene	$C_{14}H_{10}$	178·22	1·250	0·000801
2	Benzene	C_6H_6	78·11	0·879	0·00124
3	Carbazole	$C_{12}H_9N$	167·20	...	...
4	Carbon disulphide	CS_2	76·13	1·263	0·00120
5	Catechol; pyrocatechol	$C_6H_4(OH)_2$	110·11	1·344	...
6	Coumarone	C_8H_6O	118·13	1·091	...
7	*o*-Cresol	$CH_3C_6H_4OH$	108·13	1·051	...
8	*m*-Cresol	$CH_3C_6H_4OH$	108·13	1·035	...
9	*p*-Cresol	$CH_3C_6H_4OH$	108·13	1·035	...
10	Fluorene	$C_{13}H_{10}$	166·21	...	...
11	Indene	C_9H_8	116·15	1·006	...
12	Naphthalene	$C_{10}H_8$	128·16	1·14	0·000853
13	α-Naphthol	$C_{10}H_7OH$	144·16	1·285	...
14	β-Naphthol	$C_{10}H_7OH$	144·16	1·272	...
15	Phenanthrene	$C_{14}H_{10}$	178·22	1·150	...
16	Phenol	C_6H_5OH	94·11	1·073	0·00109
17	α-Picoline	$CH_3C_5H_4N$	93·12	0·945	...
18	β-Picoline	$CH_3C_5H_4N$	93·12	0·957	...
19	γ-Picoline	$CH_3C_5H_4N$	93·12	0·953	...
20	Pyridine	C_5H_5N	79·10	0·9828	0·00097
21	Quinol; hydroquinone	$C_6H_4(OH)_2$	110·11	1·358	...
22	Resorcinol	$C_6H_4(OH)_2$	110·05	1·28	...
23	Thiophen	C_4H_4S	84·13	1·065	0·00112
24	α-Thiotolen	$CH_3C_4H_3S$	98·16	1·016	...
25	β-Thiotolen	$CH_3C_4H_3S$	98·16	1·025	...
26	Toluene	$C_6H_5CH_3$	92·13	0·866	0·00110
27	*o*-Xylene	$C_6H_4(CH_3)_2$	106·16	0·880	...
28	*m*-Xylene	$C_6H_4(CH_3)_2$	106·16	0·864	0·00102
29	*p*-Xylene	$C_6H_4(CH_3)_2$	106·16	0·861	...
30	*o*-3-Xylenol (1 : 2-dimethyl-3-hydroxy-benzene)	$(CH_3)_2C_6H_3OH$	122·16	...	...
31	*o*-4-Xylenol (1 : 2-dimethyl-4-hydroxy-benzene	$(CH_3)_2C_6H_3OH$	122·16	...	...
32	*m*-2-Xylenol (1 : 3-dimethyl-2-hydroxy-benzene)	$(CH_3)_2C_6H_3OH$	122·16	...	...
33	*m*-4-Xylenol (1 : 3-dimethyl-4-hydroxy-benzene)	$(CH_3)_2C_6H_3OH$	122·16	1·026	...
34	*m*-5-Xylenol (1 : 3-dimethyl-5-hydroxy-benzene)	$(CH_3)_2C_6H_3OH$	122·16	1·016	...
35	*p*-2-Xylenol (1 : 4-dimethyl-2-hydroxy-benzene)	$(CH_3)_2C_6H_3OH$	122·16	1·026	...

Physical Constants of the More Common Constituents of Coal Tar

c = Specific heat, in g. cal./g.
l_f = Latent heat of fusion, in g. cal./g.
l_v = Latent heat of vaporization at b.p. in g. cal./g.

Note.—The following data are recommended from among those at the disposal of the Standardization of Tar Products Tests Committee in published and previously unpublished records.

No.	m.p./*c.p.*	b.p.	C.V.	*c.*	l_f.	l_v.
1	218	340	9510	0·36/120°	38·7	...
2	5·5	80·1	10030	0·406/20°	30·1	94·3
3	247	351·5	8820	...	42·1	...
4	−111·6	46·3	3240	0·240/20°	...	84
5	*105*	245	...	0·278	49·4	...
6	...	175	...	...	...	...
7	*31·0*	191·0	8146	0·497/0°-120°	...	...
8	*12·0*	202·2	8157	0·551/21°-197°	...	100·7
9	*34·7*	202·0	8152	...	26·3	...
10	116	295	9540	...	...	...
11	−2	182·4	...	...	...	...
12	80·22	218	9614	0·313/0°	35·6	75·5
13	*94*	279	...	0·388/0°	...	...
14	*122*	286	...	0·403/0°	...	...
15	101	332	9506	0·30/solid	24·2	...
16	*41·0*	181·7	7787	0·562/14°-26°	29·0	...
17	−70	128-129	8762	0·42/76°	...	90·8
18	...	143·8	8730	0·42/76°	...	96·7
19	...	143·1	8768	...	...	...
20	−42	115·3	8349	0·40/liquid	24·99	101·4
21	*170·5*	286·2	...	...	...	...
22	*110*	278·4	6210	0·269	46·2	...
23	−40	85	7975	...	14·1	...
24	−51	112	...	...	...	...
25	...	115	...	...	...	...
26	−95·0	110·5	10160	0·399/12°-99°	17·2	86·5
27	−25·7	144	10270	0·409/20°	29·3	83
28	−50	139·2	10270	0·394/20°	25·8	82
29	13·2	138·4	10270	0·398/20°	38·1	81
30	*75·0*	218·0	...	...	...	...
31	*65·0*	227·0	8480	...	...	...
32	*45·0*	201·0	...	...	...	...
33	*26·0*	211·5	8500	...	...	...
34	*64·0*	221·5	...	...	...	...
35	*75·0*	211·5	8480	...	...	...

on a sheet of asbestos having a central hole 100 mm. in diameter, but boards with central holes 30 mm. and 40 mm. in diameter, and wire gauze are severally prescribed for one or other of the Standard Methods.

(p) *Barrett Company Distillation Test for Benzole*

1. *Flask.* A 200 ml. side-neck distilling flask is specified with the side tube set so that the smaller angle where it joins the neck is 75° ±2°. The flask must be of the following dimensions :—

	Normal.	Tolerance.
Diameter of bulb (outside)	73 mm.	±1·5 mm.
Height of flask (outside)	179 ,,	±2·0 ,,
Diameter of neck (inside)	21 ,,	±1·0 ,,
Vertical distance, bottom of bulb outside, to horizontal tangent at side tube (inside)	120 ,,	±2·0 ,,
Diameter of side tube (inside)	5 ,,	±0·25 ,,
Length of side tube	127 ,,	±3·0 ,,

2. *Thermometer for use with pure benzole, toluole and xylole.* This thermometer is graduated in 0·2° from 70° to 120° for benzole and toluole and 110° to 160° for xylole. The dimensions of the thermometer are as follows :—

Total length	Not over 305 mm.
Bulb length	,, ,, 20 ,,
70° mark to bottom of bulb	80 to 100
Graduations per inch	Not over 35
Stem diameter	5 to 7 mm.
Bulb diameter	5 ,, 7 ,,

The thermometer must be accurate to 0·2° at total immersion and corrections applied according to the American Bureau of Standards' calibration. If the thermometer has a supplementary bulb situated between the lowest graduation and the main mercury reservoir, its lowest point must be not more than 1 mm. above the top of the main reservoir.

2. Physical Constants

The Standardization of Tar Products Tests Committee has surveyed the alternative data for certain of the physical properties of the more important constituents of tar, and, together with hitherto unpublished data from its own members, has prepared the schedule reproduced in the table on pp. 454-5. The data will obviously be subject to revision as alternative and additional information becomes available.

In view of the risks which would be involved, the Committee has refused to be responsible for the publication of certain types of information. Physical data for tar and impure tar fractions, such for instance as calorific values, latent heats, etc., are frequently required, for example, in the calculation of theoretical plant operations; the relationship between viscosities as determined by different instruments are often sought, as also are the relationships between the results of the several tests based on the softening of pitch. These and many other data are obviously dependent on the particular sample and, however much such data were qualified, a greater significance than they warrant would inevitably be attached to them. The references cited in the body of this volume will generally provide the information required by those who consider it, or find it, necessary to rely on data other than that resulting from tests on the particular make of product to which they wish to apply the data.

CALCIUM CARBIDE AND ACETYLENE

By C. COULSON-SMITH, M.Sc., F.I.C., Chief of Chemical and Metallurgical Section, British Oxygen Co. Ltd., London.

A. CALCIUM CARBIDE

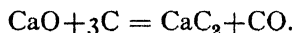
CALCIUM carbide or carbide of calcium (CaC_2, formula weight 64·08; Ca, 62·53 per cent.; C, 37·47 per cent.) is a solid of sp. gr. 2·22 at 18°, and is the only carbide used on a large scale for the manufacture of acetylene.

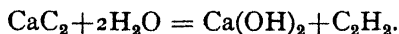
Other carbides yield acetylene when decomposed by water, *e.g.* potassium carbide, sodium carbide, lithium carbide, strontium carbide and barium carbide, but they are seldom used.

Calcium carbide was first produced in an experimental furnace at Leeds, England, and then commercially at Foyers, Inverness. The discovery of the present commercial methods for the production of calcium carbide took place at the Willson Aluminium Company, North Carolina. Willson was attempting to make metallic calcium by using a mixture of lime and coal tar in an electric furnace. He obtained a mixture which, on cooling, became crystalline and brittle, and was found to be calcium carbide; while still hot, a portion was dropped into water to ascertain whether metallic calcium had been formed. It astonished all to see that the gas evolved was ignited by the still glowing upper portion and gave off black fumes, showing that the gas was not hydrogen, which would have been liberated if calcium had been formed, but a hydrocarbon, acetylene.

At the present time, calcium carbide is produced in Norway (Hafslund, Meraker, Odda factories), France, Australia, Spain, Russia, Sweden, Dalmatia, Czecho-Slovakia, Italy, Germany, America, Canada, Switzerland, and South America.

Calcium carbide, as is well known, is produced in the electric furnace (single or 3-phase) by fusing selected grades of coal or coke and limestone together. The equation governing the reaction is as follows:—

$$CaO+3C = CaC_2+CO.$$

The carbide produced, on decomposition with water, yields *impure* acetylene gas in accordance with the following equation:—

$$CaC_2+2H_2O = Ca(OH)_2+C_2H_2.$$

The standard guaranteed yield of acetylene from commercial

calcium carbide is 4·8 cu. ft. per lb. measured dry at 15·55° and 762 mm. pressure, less 5 per cent. for inequalities, and containing not more than 0·06 per cent. by volume of phosphoretted hydrogen, and not more than 0·15 per cent. sulphuretted hydrogen by volume ; tests are also made for gaseous silicon compounds.

The impurities, both in the carbide and in the gas produced, result primarily from impurities originally in the raw materials of manufacture. Impurities occurring in calcium carbide are uncombined lime or carbon, ferrosilicon, either in lumps or small nodules or finely divided particles disseminated throughout the mass, silicon, silica, carborundum, aluminium and manganese ; apart from ferrosilicon, which varies considerably in amount, the other impurities are almost negligible in any carbide in which the limestone and coal used in manufacture are of normal good quality.

Typical analyses[1] of suitable coal, coke and limestone are as follows :—

Anthracite Coal

Moisture	=	0·90	per cent.
Phosphorus	=	0·032	,,
Sulphur	=	1·0	,,
Ash	=	3·64	,,
Volatile matter	=	5·15	,,
Fixed carbon	=	90·08	,,

Coke

Moisture	=	2·74	per cent.
Phosphorus	=	0·018	,,
Sulphur	=	0·728	,,
Ash	=	5·09	,,
Fixed carbon	=	91·4	,,

Limestone

Not more than 0·5 per cent. magnesia.
,, ,, 2·0 ,, silica.

Methods of analysis for coal and coke are given in Vol. I., p. 327 *et seq.*, and for limestone in Vol. III., p. 294 *et seq.*

Sampling of Calcium Carbide.[2]—Calcium carbide as it comes on to the market in this country is graded in sizes of: 100/200 mm., 50/80 mm., 25/80 mm., 25/50 mm., 15/25 mm., 7/15 mm., and is generally packed in 50-kilo or 100-kilo metal drums. The methods given by the British Standards Institution[3] for governing of the sale and purchase of graded carbide stipulate that, for the purpose of test, from a consignment of—

Over 60 lbs. and not exceeding	1 ton	—1 × 50 lbs. package shall be taken.
,, 1 ton ,, ,,	2 tons	—2 × 50 ,, ,, ,, ,,
,, 2 tons ,, ,,	10 ,,	—3 × 50 ,, ,, ,, ,,
,, 10 ,, ,, ,,	50 ,,	—4 × 50 ,, ,, ,, ,,
,, 50 ,, ,, ,,	100 ,,	—5 × 50 ,, ,, ,, ,,
Exceeding	100 ,,	—6 × 50 ,, ,, ,, ,,

[1] Charles Bingham, *The Manufacture of Carbide of Calcium*, 1916.

[2] Lunge and Cedercreutz, *Z. angew. Chem.*, 1897, **10**, 681 ; P. Wolff, *Z. Kalcium Karbid Fabr.*, **3**, 243 ; Odernheimer, *Chem. Zeit.*, 1902, **26**, 703.

[3] Extracted by permission from *B.S.* 642, 1935 (price 5s.).

The sampling of the requisite number of packages must be conducted in a normally dry atmosphere as expeditiously as possible and with a minimum of handling.

Method of Sampling. (1) Each package is opened separately and the sampling of that package completed before a further one is opened.

(2) The contents of each package is spread on a dry floor which is clean and sufficiently level to allow for shovelling.

(3) Approximate equal quantities are taken by means of a scoop or shovel from different positions in the spread-out carbide until an air-tight container which will hold 7 lb. is filled.

(4) The container filled with carbide is then closed.

(5) Samples from each individual package are similarly drawn, the main bulk of carbide being returned to the original packages.

Preparation of Sample for Test Purposes. If the sample pieces are above 25 mm. size they are crushed in a suitable machine (Fig. 104). It is not necessary to crush every piece completely, but it

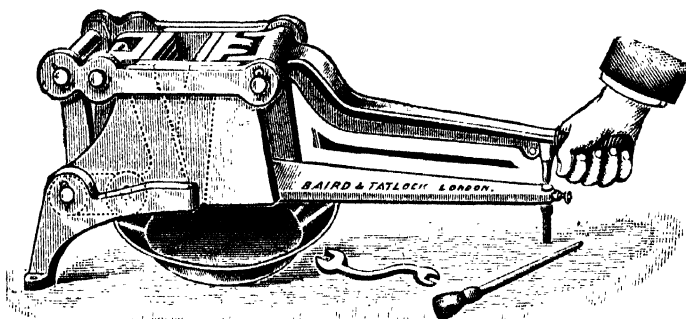



Fig. 104.

is important to get an adequate crushing from every piece above 25 mm.; an adequate crushing being one that will give from each piece above 25 mm. a representative portion which will pass through a screen of 25 mm. mesh, but which will be retained on a screen of 7 mm. mesh.

The crushings retained on the 7 mm. mesh are collected frequently and placed in an air-tight container—the small pieces which pass the 7 mm. sieve are discarded.

An average sample for testing is obtained by mixing the selected portions together, or by taking a representative quantity of the selected portions from each container.

DETERMINATION OF THE YIELD OF GAS

In accordance with the British Standards Specification,[1] the standard of gas yielded by the carbide when measured dry is as follows :—

Size.	Cu. ft./lb. at 60° F. and 30″ Hg.	Litres per kilo. at 15° C. and 760 mm. Hg.
15 to 120 mm.	4·8	300
7 „ 15 „	4·56	285
4 „ 7 „	4·32	270
2 „ 4 „	4·08	255
1 „ 2 „	3·84	240

of which 96 per cent. shall be acetylene. (The remaining 4 per cent. is mainly air.)

The determination of the gas yield is generally carried out by one of two methods—volumetric or gravimetric.

The volumetric method, although apparently simple, is liable to considerable inaccuracy unless special care is taken to verify the calibration of the volumeter at frequent intervals and also to make the necessary and proper corrections for volume at the varying pressures and temperatures recorded during the test ; in addition, a correction has to be made for the pressure of aqueous vapour present in the gas.

The gravimetric method is based on the principle originally introduced by Bamberger.[2] It is more direct, and is simple, because it reduces the matter to difference in weights, and the use of the correct value for the density of acetylene at the specified standards of temperature and pressure. The standard values of gas yield mentioned are those which have been determined by the use of the gravimetric or weight method. As a rule, impurity and gas yield tests are carried out simultaneously, using the apparatus shown in Fig. 107, p. 468. In order to make sure that all impurities liberated are absorbed a second ten-bulb tube is generally used.

In Germany the Test House (until recently under the directorship of Professor Vogel) which regulates all carbide, uses the Caro apparatus described below.

1. Caro's Volumetric Method

The apparatus shown in Fig. 105 is of the type prescribed in the regulations of the Deutsche Acetylenverein, and is similar to the one which is installed in the Central Testing Laboratories of that Association in Berlin. It operates on the " closed " system carbide-to-water principle, and is constructed to the designs of Prof. N. Caro.

This type of apparatus is considerably larger than most others, as may be judged from the fact that it has a gasholder of 400 litres

[1] Extracted by permission from *B.S.* 642, 1935 (price 5s.).

[2] *Z. angew. Chem.*, 1898, 11, 196.

(approximately 14 cu. ft.) capacity, a generator capable of taking a sample of 10 kg. (22 lb.), and weighs, without water in either the generator, washer, or gasholder, about 8 cwt. (A smaller apparatus of half the capacity is also made.) It comprises three essential parts, viz., the generating unit A, the combined washer and cooler B, and the calibrated water-sealed gasholder C. The generator A consists of a cylindrical iron vessel (1), having a detachable cover (2) and an inclined base (3), at the lowest point of which is a drain valve (4) to take off the carbide residue as sludge. In the upper part of the generator and immediately below the cover (2), which can be made gas-tight by hinged screws and wing nuts, is a series of ten wedge-

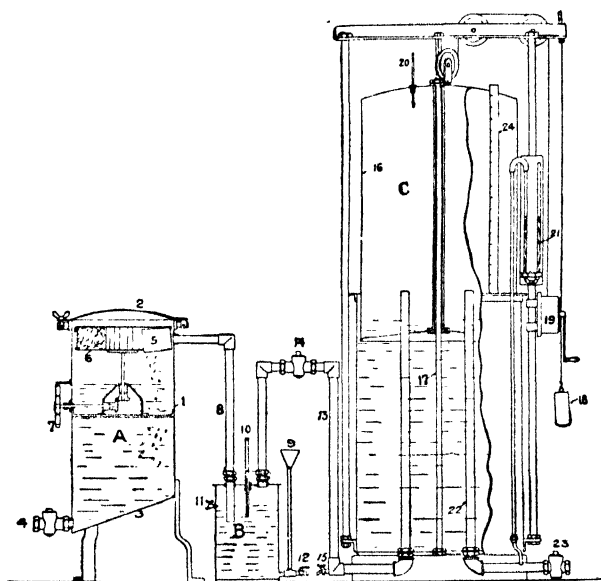



FIG. 105.—"Caro" Type Apparatus.

shaped boxes (5) which can be entirely removed from the generator when the cover is detached. These special shaped boxes have hinged covers at one end, and when filled and placed in the generator are inverted, so that a lip or extension on the hinged cover, which is now at the bottom, rests on a circular rotatable disc (6), the outer top edge of the box being hooked over a circular rail which is attached to the generator body (1). The circular disc (6) is notched out at one point so that when it is rotated by means of the external hand-wheel (7) operating through a set of bevel gears inside the generator, the lip on the hinged cover of each box is, in turn, free to pass the notch, and so deposit its contents into the water below. The external hand-wheel is suitably marked, so as to register which of the boxes is next to be emptied, and how many have been emptied. The generator is

designed to take 10 litres of water per kg. of carbide capacity; therefore, with an apparatus capable of dealing with 10 kg. of sample, the water contained in the generator would be 100 litres, in English equivalents 22 gals. of water or 1 gal. per lb. of carbide.

The generator A is connected to the combined washer and cooler B by means of a pipe (8), which dips below the surface of water contained in the washer so that the water also serves as a seal against the return of gas from the gasholder C when the generator cover is removed. The washer is fitted with a combined filling pipe and safety vent (9), and a thermometer (10), which passed through a gland in the cover and dips into the water so as to indicate its temperature. The washer is also fitted with a levelling cock (11) for fixing the height of the water and with a drain cock (12) for emptying when necessary.

The connection between the washer B and the gasholder C is made by means of the pipe (13), which is fitted with a stopcock (14) for isolating the gasholder when necessary—for example, when changing the water in the washer. The gas is conveyed to the gas-bell via the stand pipe, which passes through the mass of water in the tank of the gasholder. The pipe is fitted at its lowest point with a drain-cock (15) for drawing off any condensate. The gas-bell (16) is guided by means of a central rod (17), and is suspended from a counter-weight gear, which, in addition to being fitted with adjustable weights at (18), is arranged so that its cable passes through a hand-winch (19), which permits of the position of the gas-bell being quickly adjusted at will. Into the crown of the gas-bell and penetrating into the gas space is a suitably graduated thermometer (20), while the manometer (21), which indicates the state of pressure within the gasholder as compared with atmospheric pressure, is connected to the outlet pipe (22) from the gasholder, but for obvious reasons before the stopcock (23) thereon. The gas-bell also carries a graduated scale (24), which is calibrated to give readings to 0·5 litre, or with the use of a vernier attachment to 0·1 litre. The marker for the scale is attached to some stationary part of the gasholder, the scale moving up and down with the gas-bell, consequently the graduations on the scale number from the top downwards.

It is necessary that the water in the gasholder, washer and generator should be saturated before the apparatus is used for any actual test of gas yield. This is ensured by putting a saturating charge through the generator before the test proper is started. To do this the set of shaped boxes are removed from the generator to be cleaned and dried in preparation for taking the sample, and a single box of suitable size for the saturating charge is put into the generator, the cover put in place, and the charge dropped into the water, it being understood,

of course, that the stopcock (23) on the outlet is closed and the stopcock (14) on the inlet open, so that the gasholder takes the gas produced.

A period of some two hours is usually allowed for saturation and to allow for complete decomposition of the calcium carbide in the water, after which the gasholder is practically emptied of gas by opening the outlet cock (23), but it is advisable to leave a small quantity of gas in the holder for the final fixing of the datum point. The generator is then opened, the special box taken out and replaced by the arrangement of ten boxes in which the carefully weighed sample is distributed as evenly and as quickly as possible, after which the cover of the generator is quickly replaced and made gas-tight. The exact weight in each box is unimportant, but the total weight of the sample must be ascertained with strict accuracy. It is usual to weigh the sample to an accuracy of at least 1 in 10,000 parts. The gasholder is then brought down to the zero mark on the scale and the counterweights adjusted so that the liquid in the manometer (21) equalises, indicating that the internal pressure of the gasholder is the same as the external or atmospheric pressure. Thus prepared, the apparatus is set at its datum point.

To carry out the gas yield test the external hand-wheel (7) is turned to release the charge from the first box into the water, and the stopcock (14) being open the gas generated is collected in the gasholder. After a period of some fifteen minutes the generation of gas becomes very slow, therefore, the stopcock (14) is closed, the gas-bell quickly counterbalanced to equalise the manometer as before, the readings of the scale thermometer, and the local barometric reading recorded, whereupon the gas-bell is again emptied to the datum point, the discharge being assisted by weighting the holder from the hand-winch.

The charges in the remaining boxes are similarly dealt with in turn until the last one has been released into the generating water, when it is then necessary to allow the apparatus to stand for at least two hours, so that complete generation from all the ten charges may take place, and the water in the generator cool down, then the final reading is taken as already described.

The result of each reading is corrected to standard conditions of temperature and pressure, and average value taken as the volume of gas at standard temperature and pressure per kg. of calcium carbide.

With an apparatus of so large a size and capacity as this the percentage error on the results obtained may be relatively small by virtue of the quantities dealt with, even though the actual manipulation error is fairly large, and it is for this reason that the apparatus has been favourably received and adopted in various laboratories. On the other hand, the dimensions of the apparatus necessitate not only careful construction but extreme care during calibration. It is not

difficult to see how a very small difference in height or error in level in the position of the gas-bell can, by reason of its large area, make a very considerable difference in the recorded volume, as compared with a high lift small diameter gasholder. This type of apparatus gives satisfactory results, but moreover, the quantity of gas to be disposed of after each test, say, on 10 kg. of sample, about 3000 litres or over 100 cu. ft. of acetylene, and the space required to house the apparatus, are matters for consideration. For large works engaged in the manufacture of carbide, these are not real drawbacks, but for testing, the accepted method in this country is the gravimetric one.

The French Volumetric Apparatus—O.C.A. (L'Office Central de l'Acetylene)

The testing apparatus prescribed by the French regulations, and known as the O.C.A. apparatus, is an interesting contrast to the Caro apparatus, for while it also operates on the "closed" system carbide-to-water principle, it accommodates only a small sample and includes a small diameter high lift gas-bell for measuring the volume of gas produced.

The French apparatus, which is shown diagrammatically in Fig. 106, is of much smaller dimensions and capacity than the German apparatus, being constructed to deal with samples of only 100 g. and having a gasholder capacity of approximately 35 litres, or about 1¼ cu. ft. It consists of three main components, the generating unit A, the separator or condensation chamber B, and the water-sealed displacement gasholder E which is suitably graduated to read to 0·5 litre over a range of 35 litres or in some cases 40 litres. It will be noticed from the proportions of the gasholder that its cross-sectional area is very small in relation to its capacity, consequently the vertical list for changes in the volume of gas stored is much greater than would be the case if the gasholder was of normal proportions. The arrangement of high lift in the gas-bell makes for wide-spaced graduations and accuracy in calibration and in the reading of the scale.

The generator, although only intended for dealing with small samples, has a comparatively large water capacity which is intended to permit of several, usually five, samples being dealt with before the lime sludge is replaced with clean water.

The generator A consists of a cylindrical metal chamber (1), surmounted by the carbide hopper (2), which carries a bridge-piece and T-screw (3) for pressing the cover (4) into a gas-tight position and so sealing the generator. The carbide hopper (2) is fitted with a hinged bottom (5) which can be released from outside the generator when it is required to drop the sample into the water to start generation.

The base of the generator is fitted with a drain-cock (6) for removing the liquid sludge. The outlet from the generator is connected by means of a metal pipe (7) to the condensation chamber B, this pipe passing well down nearly to the base of the chamber. This chamber is fitted

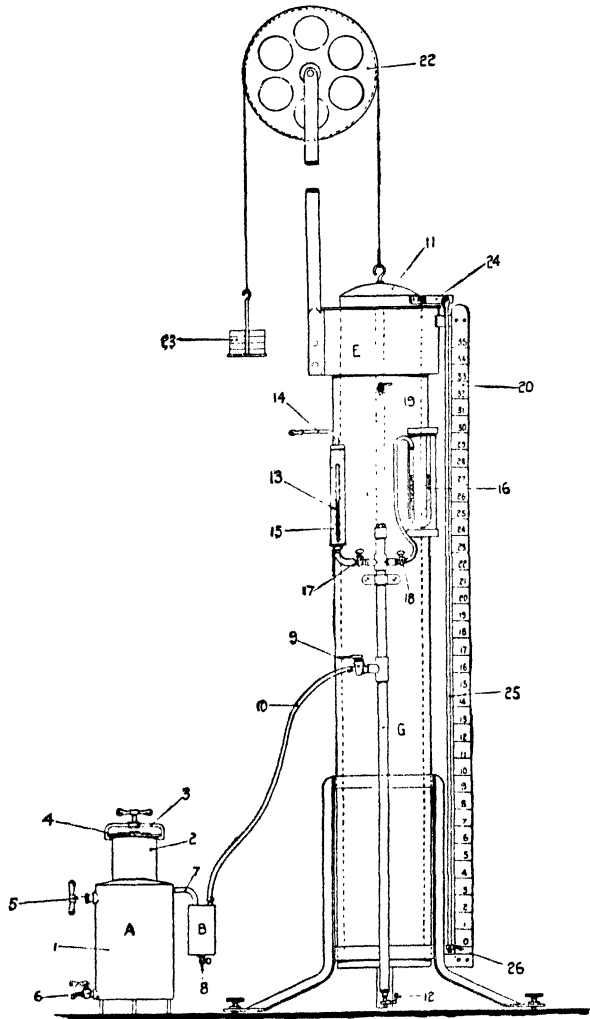



FIG. 106.—O.C.A. Type Apparatus.

at its base with a drain-cock (8) for draining off the condensate as required. The connection to the gasholder inlet cock G is made by means of a flexible rubber tube (10), so as to permit of the generator and condensation chamber being conveniently detached from the gasholder and to allow for the gasholder to be set level by means of

adjusting screws at its base, so that the gas-bell may travel throughout the full scale range without fouling the sides of the water tank. Connection is made to the gas-bell (11) by means of a stand-pipe which rises vertically from the base through the mass of water and finishes at a convenient height above the water surface. A drain-cock (12) is fitted at the lowest point in the inlet pipe to permit of draining off any condensate.

In this type of apparatus the height of the crown of the gas-bell, when fully extended, would make it inconvenient to read any thermometer attached to it, therefore the thermometer (13) is, in this case, brought to a convenient eye level by fixing it on the outlet pipe (14), and in a transparent casing (15), so that the thermometer indicates the temperature of the gas passing over it. For the same reason the manometer (16) is fixed at the same level on the casing of the water tank of the gasholder. Isolating cocks for the outlet and the manometers are provided at (17) and (18).

The water tank of the gasholder C is fitted with levelling cock (19) for fixing the height of the water therein and also carries the graduated scale (20).

The gas-bell (11) is suspended from a counterweight gear (22), which carries a scale pan (23) to accommodate the adjusting weights. Attached to the gas-bell is a bracket (24), from which is suspended a rod (25), to which is fixed at its lower end the pointer (26) registering on the scale (20).

The datum point of the apparatus is fixed in a similar manner to that previously described, that is, a saturating charge is first put into the hopper (2), the generator made gas-tight by means of the T-screw acting on the cover (4), the gas-bell lowered to the bottom, and the water level in the tank set by means of the levelling cock (19). The outlet cock (17) is then shut, and the inlet cock (9) opened, whereupon the charge is dropped into the water by releasing the bottom of the hopper (2) by means of the hand-gear outside the generator and the gas produced taken up in the gas-bell. Ample time, usually at least one hour, should be allowed for complete decomposition of the calcium carbide. The inlet cock is then closed, the hinged bottom of the carbide hopper closed, and the cover removed to take the carefully weighed sample intended for test, after insertion of which the hopper is quickly closed and sealed gas-tight. The inlet cock may then be opened and the counterweights removed from the pan, so that the apparatus is put under maximum internal pressure for location of leaks, if any, especially at the cover of the carbide hopper. After having proved the apparatus in this way, the gasholder may be emptied through the outlet, until the gas-bell comes to rest and the pressure on the two limbs of the manometer equalises. The pointer

is then set at zero on the scale, and thus the datum point for the test is fixed.

To carry out the test, the sample of carbide is dropped into the water by releasing the bottom door of the carbide hopper and sufficient time, *i.e.* at least one hour, allowed for complete decomposition of the sample. The pointer will then be towards the upper end of the scale, but before the scale reading is taken it is necessary to adjust the counterweight on the pan, so that the manometer again equalises, then the volume indicated on the scale is read off, the gas inlet immediately closed and the outlet opened, so that the gas discharge from the gasholder can, by passing over the thermometer, indicate the temperature at which it is stored at the same time as the external barometric pressure is noted, so that the volume of gas indicated by the scale can be corrected to standard temperature and pressure. It is not necessary to empty the holder entirely for this purpose if the thermometer is sensitive; moreover, it is always advisable to retain gas in the holder to ensure saturation of the water.

Some four or five consecutive tests can be made in this way before there is need to replace the water in the generator, but the generator water must be resaturated every time it is changed, though not at every test.

Determinations should always be made in duplicate and the average yield taken.

Gravimetric Method for Gas Yield (dry)

Apparatus (Fig. 107).—The generating chamber consists of a conical glass flask of about 1000 ml. capacity.

The water bath is for the purpose of keeping the generating chamber cool during the decomposition of the sample. The size of this cooling bath must be such that it is possible partly to submerge the test apparatus.

The water chamber consists of a spherical-shaped separating funnel, about 500 ml. capacity, fitted with a ground-in stopper at its upper end and a stopcock at the lower end of the bulb. The drip-tube of the funnel passes through the rubber stopper into the generating chamber. The lower end of the drip-tube is shaped and tapered to facilitate the regulation of the drip-feed of water on to the sample and to overcome the natural tendency of the water to bridge across the orifice, and thus interfere with the regular rate of feed.

The drying chamber consists of a calcium chloride tube, approximately 6 in. in length and ¾ in. in diameter, partially filled with anhydrous calcium chloride of about 14/20 mesh. This drying chamber is fixed on the outlet of the generating chamber by means

of a glass tube. Glass wool is placed at both ends of the chloride tube to prevent any loss of calcium chloride.

Fig. 107.—General Arrangement of Testing Apparatus for Determination of Gas Yield and Scheduled Impurities from Calcium Carbide.

The rest of the apparatus shown in Fig. 107 is for the estimation of impurities (see p. 475).

Method of Operation.—The water chamber is filled with water, and the drying chamber, having been charged with calcium chloride

and the two pads of glass wool, is also attached to the generating chamber and the whole accurately weighed to within 20 mg. The drip-tube of the separating funnel must be properly filled with water and the stopper fitted to the top of the separating funnel before the weighings are made.

The sample of carbide, previously graded and crushed to approximately 7/25 mm. size and to the quantity of from 200 to 250 g., is put quickly into the generating chamber with as little delay as possible, and the stopper carrying the water chamber replaced. The whole apparatus including the sample is then reweighed to the same degree of accuracy so that the exact weight of the sample of calcium carbide is obtained by difference. The apparatus as a whole is then placed in the water bath and secured.

The ground-in stopper at the upper end of the water chamber is then eased or removed in order to allow free admission of air to the water chamber. This must be done before attempting to adjust the drip-feed. The drip-feed of water is adjusted by carefully opening the stopcock on the drip-tube of the water chamber until a rate of feed of 6 or 8 drops per minute is obtained. This rate of feed is maintained without interruption until the sample is totally decomposed and generation of acetylene ceases, during which time a small jet of cooling water is fed into the water-bath and the gas produced is suitably vented to the *outside* atmosphere. The surplus water which overflows from the cooling bath is allowed to overflow and run down the outer surface of the cooling bath into a tray from which it is drained away. This assists cooling, especially at higher temperatures and where the supply of cooling water is limited.

When generation ceases the stopcock controlling the water feed is opened so that the water from the water chamber can flood in to the generating chamber, only sufficient water being retained in the drip-tube to form a seal until after weighing has been completed.

After flooding, the apparatus is allowed to stand awhile, and is then shaken gently to ensure complete decomposition of the sample. The apparatus is then removed from the water bath, carefully dried and weighed. The difference in weight thus ascertained represents the amount of gas evolved by decomposition of the sample. It is important to note that this weight represents the gas in a dry condition. Normally the time required for a complete test is from six to eight hours.

Calculation of Gas Yield

Constants

Volume of 1 g. of acetylene at S.T.P.	=	0·9014 litre.
,, ,, 1 oz. ,, ,,	=	0·9014 cu. ft.
,, ,, 1 lb. ,, ,,	=	14·43 ,,

Gas Yield in cubic feet per lb. at Standard Temperature and Pressure (B.S.I.), *i.e.* 60° F. (15·55° C.) and 30 in. (762 mm.) mercury

$$= \frac{\text{Weight of gas evolved}}{\text{Weight of } CaC_2} \times 14{\cdot}43.$$

Since		
	Molecular weight of acetylene	= 26·02.
	Density of acetylene at N.T.P.	= 1·1695 g. per litre.
	Normal temperature and pressure	= 0° C. and 760 mm.
	Standard temperature and pressure (B.S.I.)	= 15·55° C. (60° F.) and 762 mm. (30 in.).

Weight of apparatus, carbide and water, and drying tube — Weight of apparatus and water, and drying tube = Weight of carbide.

Weight of complete apparatus — Weight of exhausted apparatus = Weight of acetylene evolved.

$$\text{Volume of acetylene at } 0^\circ \text{ C. and } 760 \text{ mm.} = \frac{\text{Weight of acetylene evolved}}{\text{Density of acetylene at } 0^\circ \text{ C. and } 760 \text{ mm.}}$$

$$\text{Volume of acetylene at } 15{\cdot}55^\circ \text{ C. and } 762 \text{ mm.} = \text{Volume of acetylene at } 0^\circ \text{ C. and } 760 \text{ mm.} \times \frac{288{\cdot}55}{273} \times \frac{760}{762}.$$

$$\text{Gas yield in litres per gram at } 15{\cdot}55^\circ \text{ C. and } 762 \text{ mm.} = \frac{\text{Volume of acetylene at } 15{\cdot}55^\circ \text{ C. and } 762 \text{ mm.}}{\text{Weight of carbide}}$$

Gas Yield in cubic feet per lb. at 15·55° *C. and* 762 *mm.*

$$= \text{Gas yield in litres per gram at } 15{\cdot}55^\circ \text{ C. and } 762 \text{ mm.} \times \frac{453{\cdot}6}{28{\cdot}32}.$$

$$\therefore \text{ Volume of 1 g. of acetylene at } 0^\circ \text{ C. and } 760 \text{ mm.} = \frac{1}{1{\cdot}1695}$$

$$= 0{\cdot}855 \text{ litre.}$$

Volume of 1 g. of acetylene at 15·55° C. and 762 mm.

$$= \frac{1}{1{\cdot}1695} \times \frac{288{\cdot}55}{273} \times \frac{760}{762}$$

$$= 0{\cdot}9014 \text{ litre.}$$

Hence, Gas yield in litres per gram at 0° C. and 760 mm. $= \dfrac{\text{Weight of acetylene evolved}}{\text{Weight of carbide}} \times 0{\cdot}855.$

∴ Gas yield in cubic feet per lb. at 0° C. and 760 mm. $= \dfrac{\text{Weight of acetylene}}{\text{Weight of carbide}} \times 0{\cdot}855 \times \dfrac{453{\cdot}6}{28{\cdot}32}$

$= \dfrac{\text{Weight of acetylene evolved}}{\text{Weight of carbide}} \times 13{\cdot}70.$

Gas yield in litres per gram at 15.55° C. and 762 mm. $= \dfrac{\text{Weight of acetylene evolved}}{\text{Weight of carbide.}} \times 0{\cdot}9014.$

∴ Gas yield in cubic feet per lb. at 15·55° C. and 762 mm. $= \dfrac{\text{Weight of acetylene}}{\text{Weight of carbide}} \times 0{\cdot}9014 \times \dfrac{453{\cdot}6}{28{\cdot}32}$

$= \dfrac{\text{Weight of acetylene evolved}}{\text{Weight of carbide.}} \times 14{\cdot}43.$

Rate of Evolution of Gas and Heat of Decomposition

The rate at which acetylene is generated from calcium carbide when it is decomposed by water varies appreciably with the quality and structure of the carbide. Some makes are of dense and uniform structure throughout, whilst others are more or less porous and coke-like.

The calcium carbides which are of uniform, dense structure, and which when polished show clearly defined crystal boundaries, have a substantially uniform rate of gas generation and give a fairly consistent rise in temperature in the generating apparatus, and are therefore taken as the standard for comparison. Carbides which are not of uniform dense structure, but are porous and coke-like, are decomposed very rapidly and give rise to higher temperatures in the generating apparatus (*cf.* Figs. 108 and 109).

Samples of carbide in which the raw materials used are in disproportionate quantities, or of unsatisfactory quality, are comparatively slow in gas generation and result in a temperature rise which is below that of normal carbide. Such grades of calcium carbide are classified as " normal," " fast," and " slow " respectively.

" Fast " carbides require generally a higher proportion of water to control the temperature during generation, and usually cause a great proportion of the impurities normally soluble in the generator-water to be carried over with the gas, but they produce very little after-make of gas in the generating apparatus.

" Fast " carbides are in practice conducive to overheating in the generating chambers, especially with apparatus of the type known as the " water-to-carbide," and frequently lead to complaints regarding sandy residues, which are the result of partial polymerization of the gas during generation due to overheating of the carbide.

FIG. 108.—Dense Carbide (Polished) with Crystal Boundaries.

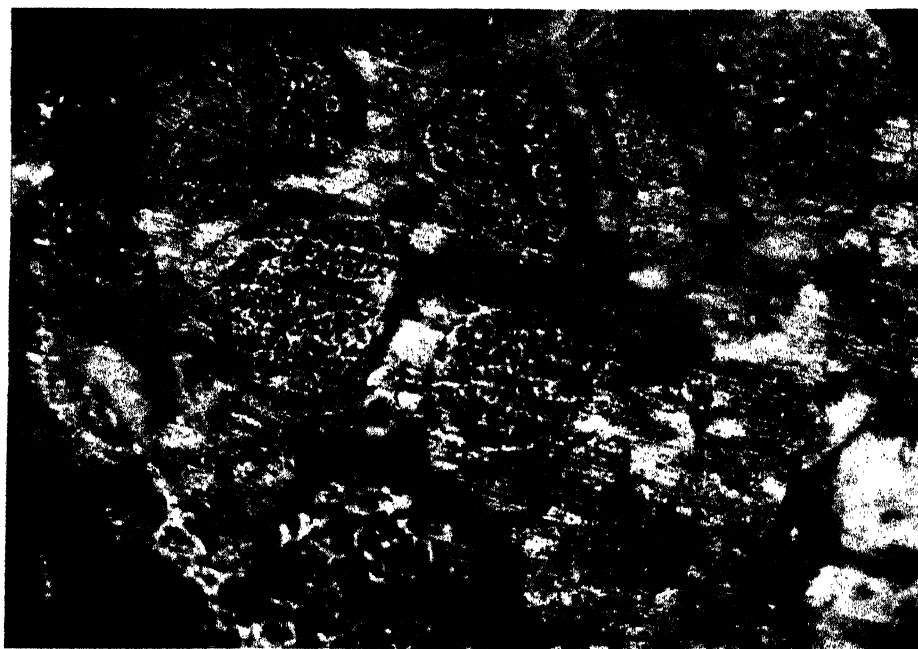



FIG. 109.—Same Specimen after one minute's exposure to Atmosphere, showing Crystal Boundary Line Attack.

"Slow" carbides are conducive to considerable after-make of gas in the generating apparatus, and generally require a larger size of apparatus for any given quantity of gas output in a given time. Moreover, they lead to waste of carbide due to incomplete decomposition in the generating apparatus, especially with that of the "water-to-carbide" type.

It is therefore important to know the comparative speeds at which the various makes of calcium carbide decompose in water and generate gas, as well as to know the rise in temperature in the apparatus or in the water contained in the generator under ordinary conditions of use.

A convenient method of determining and comparing the rate of gas generation and temperature rise is as follows :—

The apparatus (Fig. 110) consists of a wide-mouthed glass vessel of about 400 ml. capacity, fitted with a rubber stopper, perforated

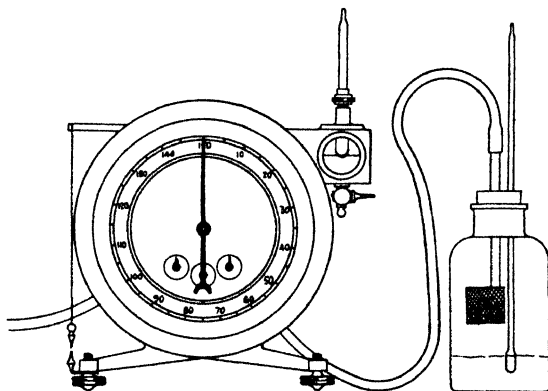



FIG. 110.—Apparatus for Determining the Rate of Generation of Acetylene from Calcium Carbide.

with three holes—one to carry the thermometer, one the gas outlet tube, and the other a glass or metal push-rod, for supporting the sample of carbide in a wire gauze basket.

50 ml. of water is introduced into the glass vessel and the temperature accurately ascertained by means of the thermometer (0°-100°), the bulb of which is placed in the water.

After crushing and sieving the carbide through a double carbide size-grading sieve (with round holes of 4 mm. minimum and 15 mm. maximum), exactly 10 g. is taken and quickly placed in the gauze basket attached to the supporting rod which passes through the rubber bung, care being taken to prevent exposure of the carbide to a moist atmosphere, and to avoid handling with moist hands. The rubber stopper supporting the thermometer and the carbide sample is then placed in the neck of the glass vessel and made gas-tight. The

gas outlet of the apparatus is then connected by means of a short rubber tube to the inlet of the gas meter. The meter and stop-watch are set at zero, and the temperature shown on the thermometer is checked.

The sample of carbide contained in the wire gauze basket is pushed down into the water by means of the push-rod passing through the rubber stopper, and generation of gas starts immediately. The glass vessel is slightly agitated to keep the water and carbide in motion until visible generation of gas ceases.

After 10 secs. the temperature as shown by the thermometer and the readings given by the gas meter are observed and recorded. This is done at frequent intervals afterwards, until visible gas generation ceases, care being taken to note the maximum rise of temperature

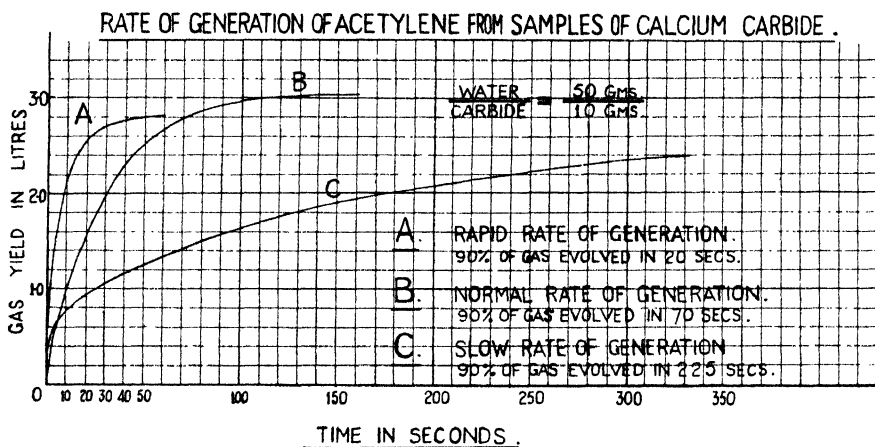



Fig. 111.

as shown by the thermometer because the temperature begins to fall off as the generation slows down.

The results of the observations are plotted on a graph to show the peak rate of gas generation and temperature rise, and these are compared with the graph relating to normal carbide. A sample graph is given in Fig. 111.

With "normal" carbide, approximately 90 per cent. of the total gas yield is evolved within the time period of 70 secs., and the corresponding temperature rise in the water is about 45° C. Visible gas generation continues up to about 160 secs. With average "fast" carbide, approximately 90 per cent. of the total gas is evolved in 35 secs. with a temperature rise of about 55° C., and visible gas generation is completed in about 80 secs. With average "slow" carbide, approximately 90 per cent. of the total gas is evolved in 225 secs., or longer, with a temperature of about 35° C.

Grades of carbide falling within these limits but approximating to one or the other of the rates given are classified under the general terms of " slow," " normal," and " fast."

B. ACETYLENE

Determination of Percentage Purity of Acetylene evolved from Calcium Carbide

The same type of apparatus is used as for the gravimetric determination of gas yield (p. 468), but with the following addition :—A length of rubber tubing is attached to the outlet from the calcium chloride tube, and the gas generated is allowed to pass through the tubing until the latter is swept free of air. The other end of the tubing is then connected to a water-filled gas sampling pipette, and a sample collected in the usual manner by displacement.

100 ml. of this sample is then drawn into an Orsat burette and the gas passed repeatedly into fuming sulphuric acid, until absorption is complete as shown by there being no further change in the reading on the burette. Before each measurement is made the gas should be passed into potassium hydroxide solution to remove the acid vapours. The residual gas insoluble in the fuming sulphuric acid is the percentage impurity in the gas under investigation.

Some chemists prefer to treat the sample successively with fuming sulphuric acid, then alkaline pyrogallol, and finally with ammoniacal cuprous chloride to remove any traces of acetylene—this the writer has not found necessary, provided that sufficient time is given for the sulphuric acid to absorb the acetylene completely. Some authors advocate the use of ammoniacal cuprous chloride solution, not only as a qualitative test, but for a quantitative determination ; this should not be used, as it is difficult to remove the bulky precipitate of copper acetylide (Cu_2C_2) completely from the glass apparatus.

As a qualitative test for acetylene a solution of ammoniacal cuprous chloride is useful and should be prepared as follows :—1 g. of copper nitrate is dissolved in a bottle in 50 ml. of distilled water, approximately 4 ml. of concentrated ammonia, 20 per cent., is added, and 3 g. of hydroxylamine hydrochloride. The solution is shaken until clear, and diluted to the mark. A red precipitate given by passing the gas under investigation denotes acetylene. The red precipitate is copper acetylide (Cu_2C_2), and as precipitated is not explosive, but readily absorbs oxygen and is then capable of detonating with explosive violence.

There are many other absorbents for acetylene, *e.g.* :—

	Investigator.
Water	Dr Krauss, Research Laboratory, Farben-industrie, Frankfurt.
Acetone-water mixture .	Dr Konschak, Reichsanstalt, Berlin.
Mercuric cyanide . .	Dr Konschak, Reichsanstalt, Berlin.
Acetone	Dr Paul Schuftan, The Linde Co., Münich.

It is obvious that solutions of mercury cyanide are somewhat dangerous to handle. The rate of solution and amount of acetylene soluble in water are so small that the author does not recommend this ; mixtures of acetone and water have been shown to give fairly accurate results, but preference is given to the use of pure acetone, as the absorbing liquid used in the apparatus, as will be described. The acetone should conform to the British Government specification.

Determination of Purity of Acetylene

Method 1. The test is carried out by taking a sample of the gas under investigation into the graduated chamber of the apparatus (Fig. 112) and passing the sample into the acetone chamber C

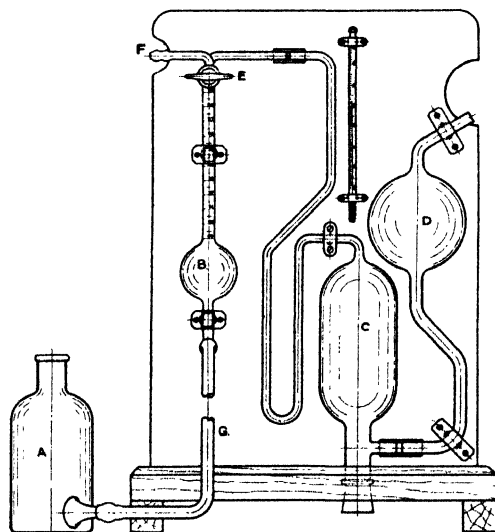



FIG. 112.—Air-Acetylene Testing Apparatus.

to absorb the acetylene, then by raising the levelling bottle A the gas is brought back into the graduated chamber and so on until a constant level is obtained. The proportion which is not absorbed by the acetone indicates the percentage of air and impurities in the gas. In addition, this amount will contain some acetone vapour

for which due allowance must be made at the existing temperature, taken on the thermometer affixed to the apparatus boards. The unabsorbed volume is then multiplied by the factor to arrive at the correct percentage purity.

Table showing Vapour Pressure of Acetone * at Temperatures from 0° C. to 30° C.

Temperature.	Vapour pressure.	Correction factor.	Temperature.	Vapour pressure.	Correction factor.
° C.	mm. Hg.		° C.	mm. Hg.	
0	75	0·9014	16	154	0·7975
1	77·5	0·8980	17	161	0·7881
2	80	0·8948	18	168	0·7789
3	83	0·8908	19	176	0·7685
4	87	0·8855	20	186	0·7553
5	91	0·8808	21	195	0·7443
6	95	0·8750	22	205	0·7303
7	100	0·8684	23	214	0·7185
8	105	0·8618	24	223	0·7066
9	110	0·8553	25	232	0·6947
10	116	0·8471	26	242	0·6816
11	122	0·8395	27	252·5	0·6677
12	128	0·8316	28	262·5	0·6546
13	134	0·8237	29	272·5	0·6413
14	141	0·8145	30	283	0·6276
15	148	0·8054	...	...	...

* Compiled from graph based upon data in *The Chemists' Year Book*, 1931, pp. 138-141.

Method 2. A method is sometimes used which is very simple but not quite so accurate, and is carried out in a single absorption tube with a levelling bottle to adjust the final pressure (Fig. 113).

The sample tube filled with water is taken and affixed by means of a rubber tube to the gas supply. The cocks are opened and the water displaced ; the gas is allowed to pass through the tube for at least 60 secs. After this displacement has taken place, the rate of gas flow is kept as low as possible. Having now passed the gas through, the supply cock is shut, the tap on the gas sampling tube on the inlet end, and finally that on the outlet end. This is done quickly in order to prevent any excess pressure above atmospheric in the sample tube, or backward diffusion of air. The tube is then taken and acetone of standard quality, which has not previously been saturated with acetylene, admitted. This is done by immersing the inlet stem of the sampling tube in acetone and opening the cock, or by using the levelling bottle which is filled with acetone and is used for producing a static head of pressure. Originally this type of apparatus was used but modified as shown in Fig. 114, the air bulb being used to exert an initial pressure on the surface of the acetone and thereby causing it to rise up the capillary tube into the chamber itself. The results obtained

were slightly inaccurate on account of the operator being unable to adjust the final pressure.

When inrush of acetone has ceased, the cock is closed and the sample tube shaken, both stems being held and care being taken to avoid undue handling which would tend to raise its temperature.

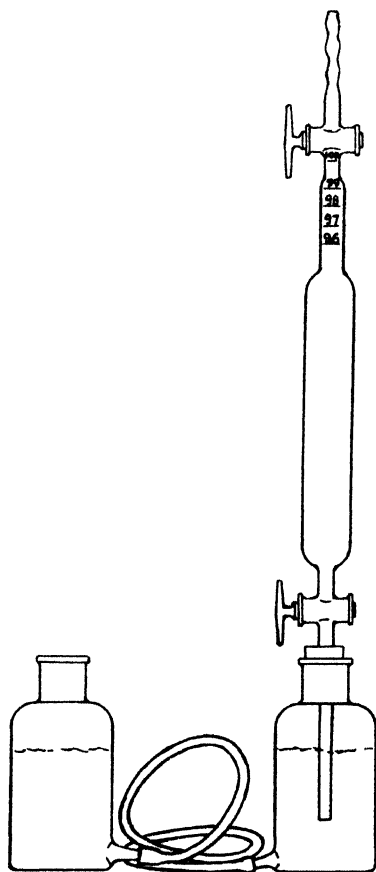



FIG. 113.—Determination of Purity of Acetylene. Method 2.

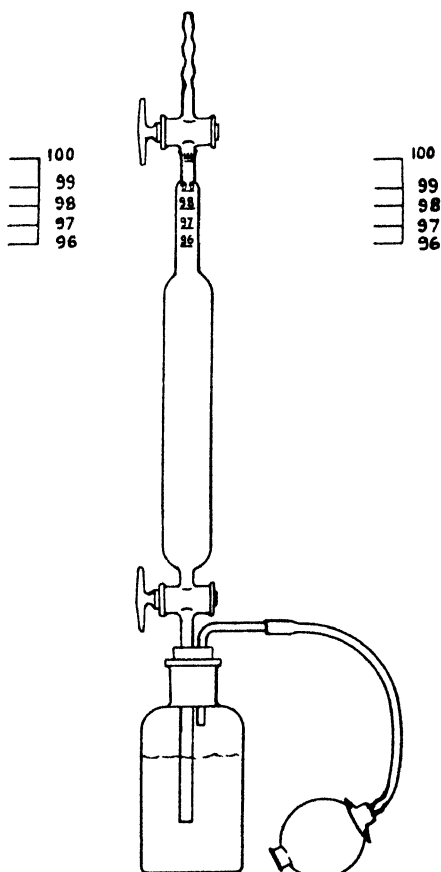



FIG. 114.—Original Apparatus for Determination of Purity of Acetylene.

The acetone injection process is repeated until a constant reading is obtained.

The result is then read off on the graduated scale of the burette, which is calibrated in direct percentages. The result has to be corrected for the vapour pressure of acetone at the temperature at which the test was made, in accordance with the table on p. 477.

Method 3. A very recent form of apparatus, using acetone as the absorbent and requiring a minimum of handling, is shown in Fig. 115.

The tube W is filled with water, and K and M with acetone. The

graduated chamber H is now filled by opening cocks A, C, and D. Water runs from W into H and when full, out at O; cocks A and C are then closed. The gas under investigation is brought into H by connecting a piece of rubber tubing to O and opening A and C. The water is then displaced into the water cup through G. After the passage of gas for 60 secs. following the displacement of the water, A, C and D are closed, and the cock C opened to connect with K; inrush of acetone takes place and continues until *almost* complete absorption of the acetylene is obtained. In order to obtain final absorption C is closed and tap A opened to connect with M. When absorption is complete, no further acetone will rise in H. The tap A is closed, the reading noted and correction for the vapour pressure of acetone existing at the temperature is made from the table on p. 477. Having now made the test, the acetone is run out by opening cocks A, C, and D, and the tube H can be refilled as before in readiness for a further test.

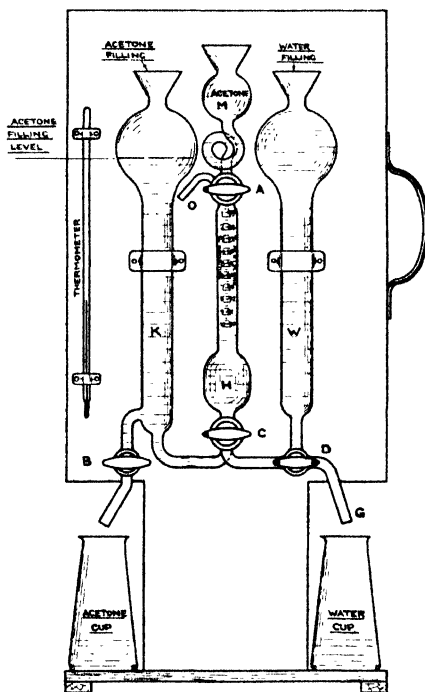



FIG. 115.—Absorption Apparatus for Acetylene.

For laboratory tests this type of apparatus is ideal, but is somewhat delicate for plant operators.

Determination of Impurities in Acetylene evolved from Calcium Carbide

The scheduled injurious impurities in acetylene with their limits according to the British Standard are:—

	Per cent. by volume.
Phosphorus compounds (calculated and expressed as PH_3) .	0·06
Sulphur compounds (calculated and expressed as H_2S) .	0·15

Other less important impurities are carbon dioxide, ammonia, and moisture. There is no limiting standard for these impurities as governed by the British Standards Institution or the British Acetylene Association, but War Office and Admiralty specifications demand that the CO_2 shall not be greater than 0·05 per cent. by volume, the

NH_3 shall not be greater than 0·02 per cent. by volume, and the H_2O shall not be greater than 0·25 per cent. by weight.

As a rule, approximately 70 g. of calcium carbide is taken for the decomposition. The calcium chloride drying chamber is connected by means of rubber tubing to two ten-bulb tubes containing sodium hypochlorite having a minimum chlorine content of 3 per cent. (see Fig. 107, p. 468). A blank sulphur and phosphorus determination is carried out on the hypochlorite solution prior to any test, and allowance made when expressing the results.

Sulphur Compounds.—On completion of the decomposition of the sample, the ten-bulb tubes containing the sodium hypochlorite are disconnected and the solution transferred to a beaker and boiled free of acetylene. It is then oxidised with 10 ml. of concentrated nitric acid. The addition of the acid must be made cautiously and little by little. The solution is then boiled, evaporated to dryness, cooled, water added, and the liquid acidified with hydrochloric acid. The silica is filtered off and the sulphur compounds then precipitated by the addition of a 10 per cent. solution of barium chloride. This solution is allowed to stand for at least six hours in order to obtain complete precipitation of the barium sulphate. The solution is filtered, the barium sulphate washed free from chlorides, ignited and weighed. The weight obtained is converted into percentage by volume of H_2S in the gas evolved, as follows :—

$$\text{Per cent. by volume of } H_2S = \frac{\text{weight of } BaSO_4}{\text{weight of gas evolved}} \times 11{\cdot}25.$$

The factor 11·25 is arrived at as follows :

$$\text{Weight of barium sulphate} = B \text{ g.}$$

$$\text{Weight of gas evolved} = W \text{ g.}$$

$$\text{Weight of } H_2S \text{ gas evolved} = \frac{0{\cdot}1374 \times B \times 34}{32}$$

$$\text{Volume of } H_2S \text{ at } 0^\circ \text{ C. and 760 mm.} = \frac{0{\cdot}1374 \times B \times 34 \times 22400 \text{ mls.}}{32 \times 34}$$

$$= \frac{0{\cdot}1374 \times B \times 22400 \text{ mls.}}{32}$$

$$\text{Per cent. by volume } H_2S = \frac{0{\cdot}1374 \times B \times 22400 \times 100 \times 1{\cdot}1695}{32 \times W \times 1000}$$

$$\text{Per cent. by volume } H_2S = \frac{0{\cdot}1374 \times B \times 2240 \times 1{\cdot}1695}{32 \times W} = \frac{B}{W} \times 11{\cdot}25.$$

Phosphorus Compounds.—The filtrate from the sulphur determination is used for the determination of the phosphorus. There are various methods for this, using magnesium pyrophosphate, ammonium

phosphomolybdate, or lead molybdate as the means of determining the phosphorus.

Method 1. The phosphorus compounds are precipitated in the usual way by magnesia mixture. The magnesium pyrophosphate is filtered, dried, ignited, and weighed. The weight of magnesium pyrophosphate thus ascertained is converted into percentage by volume of phosphoretted hydrogen in the gas passed.

$$\text{Percentage of } PH_3 \text{ by volume at } 0° \text{ and } 760 \text{ mm.} = \frac{23{\cdot}55 \times M}{W}$$

where M = weight of pyrophosphate precipitated, and W = weight of gas evolved.

$$\text{Since} \qquad P = 0{\cdot}2787 \times M,$$

$$\text{Weight of } PH_3 \text{ (gas)} = \frac{(0{\cdot}2787 \times M)}{31} \times 34$$

$$\text{Volume of } PH_3 \text{ (gas) at } 0° \text{ and } 760 \text{ mm.} = \frac{0{\cdot}2787M \times 34 \times 22400}{31 \times 34}$$

$$\text{Per cent. } PH_3 \text{ by volume at } 0° \text{ and } 760 \text{ mm.} = \frac{0{\cdot}2787M \times 22400 \times 1{\cdot}1695 \times 100}{31 \times W \times 1000}$$

$$= \frac{23{\cdot}55 \times M}{W}.$$

Method 2. The filtrate from the sulphur determination is neutralized with ammonia, then made slightly acid with nitric acid, and heated to 70°, at which temperature 30 ml. of ammonium molybdate solution is added. The solution is then allowed to stand on a warm plate for an hour to obtain complete precipitation of the phosphomolybdate. This precipitate is then transferred to a Gooch crucible, washed with a 1 per cent. solution of nitric acid and finally washed free of acid with a 1 per cent. solution of potassium nitrate. The precipitate is then transferred to a beaker and dissolved in 25 ml. of $N/5$ sodium hydroxide and the excess titrated by $N/5$ sulphuric acid, using phenolphthalein as internal indicator.

The ammonium molybdate solution is prepared by dissolving 50 g. of ammonium molybdate in 100 ml. of distilled water, adding 100 ml. of 0·88 ammonia and pouring slowly (keeping cool) into 750 ml. of nitric acid (1·2 sp. gr.). The solution is allowed to stand for approximately three hours. If any precipitate is apparent after this period, the solution should be filtered before use.

$$\text{Percentage by volume of } PH_3 = \frac{(b-c)N \times 0{\cdot}1139}{5W}, \text{ where}$$

W = weight of gas evolved,
b = ml. of standard H_2SO_4 = total NaOH used,
N = normality factor of standard acid,
c = ml. of standard acid = excess NaOH.

The factor 0·1139 is obtained as follows :—

$$\text{Weight of phosphorus} = (b-c)\text{N} \times 0{\cdot}001348 \text{ g.}$$

$$\text{Weight of PH}_3 \text{ (gas)} = \frac{(b-c)\text{N} \times 0{\cdot}001348 \times 34 \text{ g.}}{31 \times 5}$$

Volume of PH_3 gas at 0° C. and 760 mm.

$$= \frac{(b-c)\text{N} \times 0{\cdot}001348 \times 34 \times 22400 \text{ mls.}}{31 \times 34 \times 5}$$

$$= \frac{(b-c)\text{N} \times 0{\cdot}001348 \times 22400}{31 \times 5}$$

$$\text{Per cent. of PH}_3 \text{ gas} = \frac{(b-c)\text{N} \times 0{\cdot}001348 \times 2240 \times 1{\cdot}1695}{31 \times \text{W} \times 5},$$

Method 3. After filtration of the $BaSO_4$, the filtrate is neutralized with ammonia, made slightly acid with nitric acid and warmed to 70°, 30 ml. of ammonium molybdate solution then added, and the solution allowed to stand on a hot-plate for an hour. When precipitation of the phosphomolybdate is complete it is transferred to a Gooch crucible and washed with a 2 per cent. solution of nitric acid.

In order to convert this precipitate to its equivalent of lead molybdate, it is extracted with a few millilitres of ammonia ; the ammoniacal solution is then heated to boiling and carefully acidified with hydrochloric acid in order to keep the lead molybdate and phosphate in solution. Next, lead acetate solution in sufficient quantity to combine with the molybdic and phosphoric acids present is added. The solution is now poured into boiling ammonium acetate (150 ml.) containing 10 g. of ammonium chloride. This removes excess acid, lead molybdate is precipitated, allowed to settle out, filtered through paper pulp, washed with hot water, ignited wet, and weighed as lead molybdate, $PbMoO_4$.

Expressing results,

$$\text{Per cent. of PH}_3 \text{ by vol.} = \frac{\text{Weight of PbMoO}_4}{\text{Weight of gas evolved}} \times 0{\cdot}005393.$$

The author has carried out many analyses and for speed and accuracy prefers the titrimetric method.

H. R. Granjon gives the following solution [1] :—Mercuric chloride, 10 g. ; potassium chloride, 20 g. ; distilled water, 1 litre. The test is carried out by bubbling a metered volume of impure acetylene gas through 10 ml. of solution. Phosphine gives a yellow precipitate darkening to orange, while hydrogen sulphide gives a voluminous black precipitate, both settling on standing. Impure acetylene gives at first a faint opalescence, changing to a yellow precipitate after prolonged passage of the gas. If the acetylene is rich in PH_3, this

[1] "Rapid Estimation of Phosphuretted Hydrogen in Acetylene," *Congrès Int. d'Acétylène*, Brussels, 1927.

is a good qualitative test, but is of little value in gas which only contains traces, because of confusion with traces of other impurities.

The determination of phosphorus compounds has been dealt with at length, on account of the importance of this impurity; for many explosions which have been classified as acetylene explosions have not been due in the first place to acetylene, but to mixtures of acetylene with air or the spontaneously ignitible hydride of phosphorus, P_2H_4, sometimes in generators and in cylinders, or even on opening drums of carbide to which, by chance, moisture has had access.

Silicon Compounds.—These impurities comprise various hydrides of silicon. The method of determination is that formulated by Caro. He suggested a dome of platinum or pure nickel, the latter being preferred by the present author; many tests checked by a public analyst and

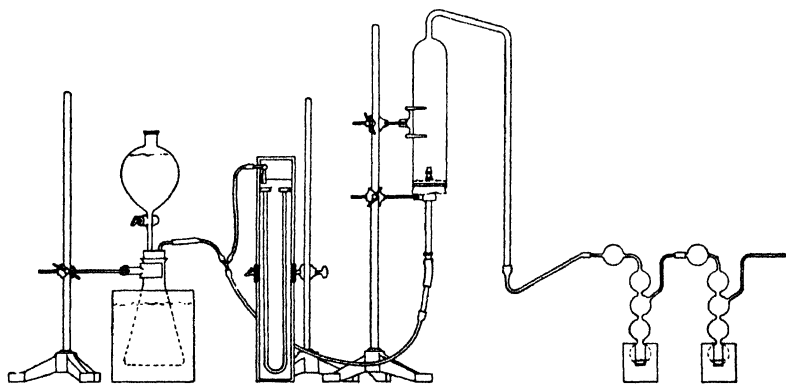



FIG. 116.—Determination of Silicon Compounds in Acetylene.

other independent chemists have shown that, with care, using a Pyrex glass dome and wash-bottles, results in very close approximation to each other are obtainable.

The apparatus used is as shown in Fig. 116. The acetylene is generated in a similar apparatus to that used in the determination of gas yield, the carbide being that which is suspected of containing silicon. No calcium chloride dryer is necessary.

From the generator the gas is led to a manometer and to a calibrated burner (Fig. 116) which is fixed in the correct position under the glass dome. The orifice of the dome is protected from ingress of dust, etc., by covering it with a piece of fine mesh muslin. The dome is connected to two wash-bottles, each containing a 10 per cent. solution of sodium hydroxide (prepared from pure sodium). Air is drawn through the system by means of a pump. Approximately 50 litres of acetylene is burnt, the approximate consumption oft he burner being 3 litres per hour.

At the end of the test the number of hours of burning is noted and

the pressure taken every half hour during the test. The average amount of gas passed is arrived at by means of a graph, prepared during the calibration of the burner. The requisite number of litres of gas under investigation having been burnt, the dome is disconnected and washed with the 10 per cent. solution of sodium hydroxide. To this solution is added the solution from the wash-bottles, the whole made acid with hydrochloric acid, evaporated to dryness and the residue baked. This residue is taken up in 1 : 1 hydrochloric acid and the silica filtered, washed, ignited and weighed in a platinum crucible, the weight being checked by treatment with hydrofluoric acid.

For the necessary blank determination the clean dry dome is washed out with the same quality of 10 per cent. sodium hydroxide solution as is used in the actual estimation. To this solution is added sodium hydroxide solution equal in quantity and concentration to that used with the wash-bottles and in the estimation. The total silica in the combined solution is weighed and deducted from the weight of silica obtained in the estimation. The sodium hydroxide used in the blank test is kept in contact with the wash-bottles for a period equal to that of the actual estimation.

The loss in weight in actual determinations, even after fourteen hours contact of 10 per cent. sodium hydroxide with the Pyrex apparatus used at 15° is only 6×10^{-6} g. per sq. cm.

Calculation of Results—

Density of silane (SiH_4)	1·44 g./litre
Density of acetylene (C_2H_2)	1·1695 g./litre

$$\text{Per cent. by volume of } SiH_4 \text{ in acetylene at N.T.P.} = \frac{\text{Volume of } SiH_4}{\text{Volume of } C_2H_2} \times 100.$$

$$= \frac{\text{Weight of } SiH_4 \times 100}{1 \cdot 44 \times \text{volume } C_2H_2}$$

$$= \frac{0 \cdot 53 \times \text{weight of } SiO_2 \times 100}{1 \cdot 44 \times \text{volume } C_2H_2}$$

$$= \frac{\text{Weight of } SiO_2 \times 36 \cdot 8}{\text{Volume of } C_2H_2}.$$

Originally a wet meter was used to measure the gas, but owing to the considerable solubility of the silicon compounds in the water of the meter, low results were obtained. The apparatus was therefore modified by the substitution of a calibrated burner for the wet meter.

Like phosphorus compounds, gaseous silicon compounds have been suspected of spontaneous ignition and the resultant explosion of acetylene when brought into contact with air; hence it is advisable to test for this impurity, cf. *British Standards Institution*, *B.S.* 642, 1935 (price 5s.).

Estimation of Carbon Dioxide, Ammonia, and Moisture

As a rule these impurities are not considered important, but the method of their determination as carried out at the laboratory of the British Oxygen Co. Ltd., in conjunction with the other more important scheduled impurities, is as follows.

The apparatus used is a composite one, capable of being carried to various parts of the gas service, and is shown in Fig. 117. It consists of :—

A. A Wöhler type absorption tube containing anhydrous calcium chloride for the absorption of moisture.

B. A Mohr type absorption tube for carbon dioxide (and H_2S) determination containing a solution of potassium hydroxide with a calcium chloride dryer on the outlet.

C. A White's type of absorption tube for ammonia estimation, containing standard hydrochloric acid.

D. A White's type of absorption tube containing 75 mls. of sodium hypochlorite for extraction of PH_3 and H_2S (NaClO—chlorine content not less than 3 per cent.).

E. A water U-tube manometer.

F. A wet meter.

The gas under investigation is led into A and the moisture is determined by the increase in weight of tube A. Prior to the initial weighing, any air contained in the tube A is completely displaced by acetylene. Carbon dioxide is estimated from the increase in weight of tube B, allowance being made for hydrogen sulphide subsequently determined in the potassium hydroxide solution. Prior to the initial weighing, any air contained in tube B is displaced by acetylene. Ammonia is estimated by titration of the excess acid remaining in the solution in tube C using $N/100$ NaOH or by Nesslerising. The PH_3 is estimated in the solution contained in D, by the method already given.

Where it is inconvenient to have a large wet meter, a very convenient form of apparatus[1] which can be utilised is that developed by E. G. Beckett,[2] as shown in Fig. 118.

The diagram shows the design of the apparatus. It is filled up to the dotted line AB with water, which thus fills the siphon C connecting the two limbs of the U-tube. When the gas to be measured enters the apparatus, it forces the level of the water down in A and up in B, until the difference in pressure causes the siphon C to empty

[1] It can be procured from Messrs Baird & Tatlock, London.

[2] *J. Soc. Chem. Ind.*, 1917, **36**, 52.

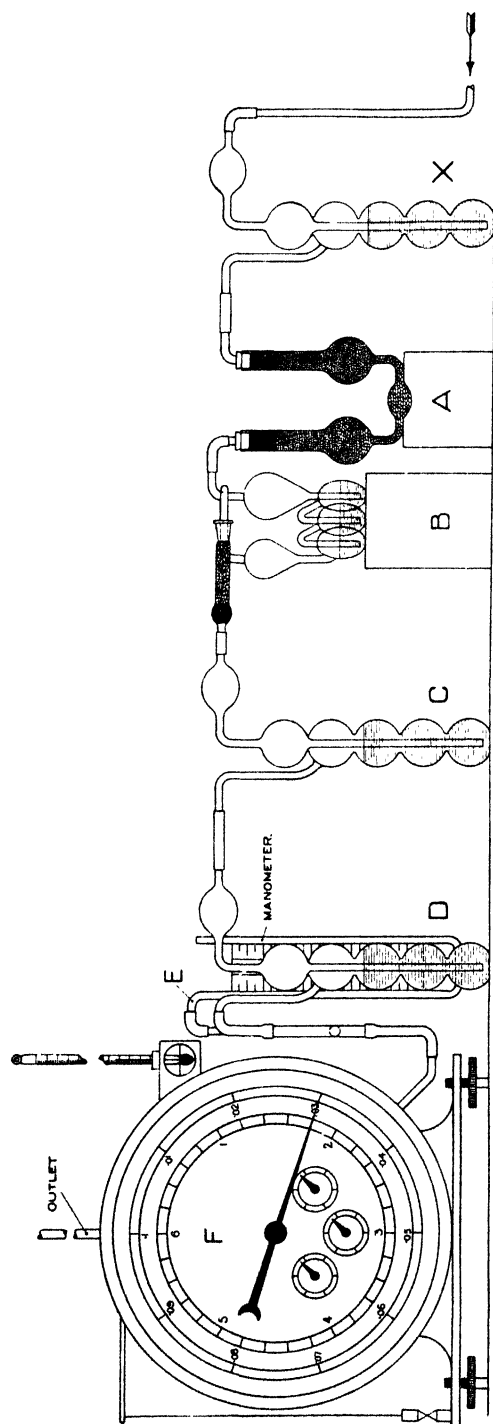



Fig. 117.—Diagrammatic Arrangement of Gas Testing Apparatus.

itself into B. The gas in A then escapes into B through the siphon, while the level of the water readjusts itself in the U-tube and again fills the siphon C. The process then starts again. The siphon runs over each time after a definite amount of the gas has passed through the instrument; the amount, however, varies with the velocity of the gas. A determination of the capacity of the gas meter for different velocities gave the following results :—

Rate c.c. per sec.	Capacity in c.c.
15·5	44·5
10·0	42·5
7·61	40·5
3·56	40·0
3·75	37·5
1·93	36·5
0·54	35·4

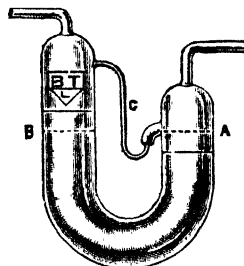



Fig. 118.

As this siphon gas meter is made entirely of glass, it may be used for any gas which is but slightly soluble in water or in the liquid used. It is also useful for highly corrosive gases, such as chlorine, for which the ordinary metallic gas meter is out of the question.

If a constant stream is desired, gas at a high pressure should be employed and the rate regulated or throttled immediately in front of the gas meter. For gases very soluble in water other liquids have to be used instead, but only mobile liquids can be employed.

For other tests for impurities in acetylene, see Lunge and Ambler, *Technical Gas Analysis*, London, 1933, p. 262 *et seq.*

Commercial Purification of Acetylene

Many types of purifying materials have been manufactured, such as Frankoline, Klenzol, Catalysol, Alpurene and Regenetal. The majority of these have either a chromic acid base or are a ferric-oxy-chloride, or a bleaching-powder mixture, their main function being that of oxidising the various impurities and fixing them in the material. Of all these the chromic acid and ferric-oxychloride materials have proved superior, especially when absorbed in a high grade, preferably calcined, kieselguhr, which, with a silica content of 96 per cent., is very absorbent and holds a considerably greater amount of active chemical solution than other grades of kieselguhr of the same silica content.

Where the gas is to be compressed for storage as "dissolved acetylene," the greater part of the impurities are removed (1) by partial retention in the water of decomposition, (2) in the washers following the generators in the plant system, (3) in the chemical purifiers, (4) in

the low-pressure dryers, (5) in the stages of compression, (6) in the final high-pressure dryers.

Estimation of Acetone Vapour in Acetylene from a Dissolved Acetylene Cylinder

Sometimes in making gas analyses on dissolved acetylene, *i.e.* compressed acetylene in cylinders containing porous mass and acetone, it is necessary to make a determination of the acetone which comes off in vapour with the gas. The method used for this determination is as follows :—

Gas from the cylinder under test is passed for a convenient period at a rate of 10 litres per hour through a wash-bottle containing 50 ml. of $N/10$ iodine and 25 ml. N sodium hydroxide. After passage of the gas, the wash-bottle is removed, set aside for ten to fifteen minutes and about 25 ml. of N sulphuric acid added to make the solution just acid.

The excess of iodine is then determined by titration with $N/10$ sodium thiosulphate solution, using starch solution as indicator ; 1 ml. $N/10$ iodine $= 0{\cdot}967$ mg. acetone. If x ml. $N/10$ iodine was used up by the acetone in V litres of gas, then the weight of acetone in V litres $= 0{\cdot}000967x$ g.

$$\text{Volume of acetone} = \frac{22{\cdot}4 \times 0{\cdot}000967x}{58} \text{ litres.}$$

$$\text{Percentage by volume of acetone in the gas} = \frac{22{\cdot}4 \times 0{\cdot}000967x \times 100}{58V}.$$

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EXPLOSIVES

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MOST explosives consist either of a mixture of carbon compounds with compounds rich in oxygen, or of organic compounds such as nitro-compounds and nitric esters, which contain the oxygen necessary for their combustion. A smaller class of explosives includes substances which undergo exothermic decomposition. The materials to be tested comprise oxidising agents such as nitrates and chlorates, reducing agents such as carbon, sulphur and organic compounds; nitro-compounds, nitric esters and the raw materials required for their manufacture, solvents, stabilisers, and a variety of other ingredients. The increasing use of non-volatile solvents, such as centralite, and the production of smokeless, non-flash and non-hygroscopic explosives has extended the range of analytical tests in the examination of explosives.

This section deals mainly with chemical and stability tests. Physical and explosive tests are treated very briefly and special treatises should be referred to for fuller details of these tests (see Literature, p. 581).

A. INGREDIENTS AND RAW MATERIALS

I. NITRATES

(a) Potassium Nitrate

Mol. wt., 101·1; sp. gr., 2·109; M.P., 337°; decomp. at 400°; soluble in 100 parts water, 13·2 at 0°, 246 at 100°.

The nitre which reaches explosives factories is usually refined. For crude nitre see Vol. II., p. 420.

Moisture. A weighed quantity is heated in a platinum crucible until it just melts, cooled in a desiccator and again weighed. The moisture should not as a rule exceed 0·05 per cent. Limits ranging from 0·03 to 0·25 per cent. are specified in different countries.

Insoluble in Water. This is determined in the usual way and should be practically nil.

Chlorides. A qualitative test with silver nitrate is usually sufficient. If necessary, the turbidity is compared with that produced by a known amount of chloride. Specification limits vary from 0·005

to about 0·03 per cent. For the quantitative estimation, the silver chloride may be weighed, or the chloride may be determined by titration with silver nitrate, using potassium chromate as indicator.

Sulphates. These are estimated as barium sulphate and should not exceed 0·1 per cent. (as K_2SO_4).

Perchlorates. These may be present in appreciable quantity in conversion-saltpetre. The following method[1] gives very accurate results : 20 g. of the sample is heated to 545° in a covered nickel crucible and maintained for an hour at this temperature in a Gilbert furnace or electric furnace, to reduce the perchlorate to chloride, which is then titrated with silver nitrate by Mohr's or Volhard's method. The chloride present in an unheated sample is deducted. Any chlorate or iodate present must also be allowed for. Lenze[2] recommended heating for half an hour in a porcelain crucible at 580° to 600°. The first quarter of an hour is occupied in raising the temperature to the required point. At higher temperatures losses of chloride occur. A method based on the same principle is given by Taylor and Rinkenbach.[3] Methods involving the addition of iron filings, manganese dioxide, sodium bicarbonate, etc., have been proposed, but appear to have no appreciable advantage. Leimbach[4] has proposed a wet method depending on precipitation with nitron, after removing the nitrate and chlorate by heating with hydrochloric acid. Reduction of the perchlorate with titanous sulphate has also been recommended.[5]

A review of the methods has been given by Junk.[6] Specification limits from 0·1 to 0·3 per cent. are given ; potassium nitrate containing nitrites under 0·5 per cent. did not increase the sensitiveness of gun-powder and synthetic nitrates were found to be as suitable as material prepared from Chili nitrates. Dupré[7] gave limits for the amount of perchlorate permissible in nitre for the manufacture of gun-powder.

Chlorates. Traces of chlorate give a yellow colour when the salt-petre is added to concentrated sulphuric acid. This can be used roughly as a colorimetric method. Another sensitive test[8] depends upon the formation of a blue colour by aniline hydrochloride in concentrated hydrochloric acid. Chlorates can also be reduced to chloride by zinc, iron, formaldehyde, sulphurous acid, etc. The

[1] Dupré, *J. Soc. Chem. Ind.*, 1902, **21**, 825.
[2] *Int. Congr. Appl. Chem.* V., 1903, **2**, 394.
[3] *U.S. Bur. Mines, Bull.* **219**, 1923, 17.
[4] *Z. angew. Chem.*, 1926, **39**, 432.
[5] Rothmund, *Z. anorg. Chem.*, 1909, **62**, 108 ; König, *ibid.*, 1922, **120**, 48.
[6] *Z. ges. Schiess- u. Sprengstoffw.*, 1922, **17**, 1.
[7] *Loc. cit., cf.* also Lenze and Bergman, *Int. Congr. Appl. Chem.*, 1904, **2**, 394.
[8] Lafitte, *Int. Congr. Appl. Chem.* V., 1903, **1**, 311 ; Virgili, *Rev. R. Acad. Cienc. Madrid*, 1908, **7**, 884 ; 1909, **8**, 329.

chloride is then determined by filtration, using Volhard's method. Hendrixson [1] describes a method based on reduction with iron. In most specifications chlorates are excluded entirely. Sometimes 0·01 per cent. is admitted.

Saltpetre is also tested for carbonates, sodium, calcium and magnesium salts, and nitrites. These should be practically absent.

Potassium nitrate which is made from synthetic nitric acid, either by direct neutralization with potassium carbonate, or through the sodium salt, is very pure and in general it suffices to test for moisture, insoluble matter, chloride and chlorate.

The moisture content is generally less than 0·1 per cent. and the impurities are present only in traces.

Estimation of Potassium Nitrate. Potassium nitrate is readily determined in gun-powder and allied mixtures by extraction with water.[2] The nitrate may be determined, if necessary, by means of the Lunge nitrometer, the Schulze-Tiemann test or by precipitation with nitron.[3]

(b) Sodium Nitrate

Mol. wt., 85·0; sp. gr., 2·26; M.P., 312°; soluble in 100 parts water, 73 at 0°, 175 at 100°; slightly soluble in alcohol.

The requirements of sodium nitrate for the manufacture of nitric acid are given in Vol. I., p. 470. Sodium nitrate for explosive purposes may be tested for moisture, insoluble matter, potassium, calcium, chloride, sulphate and sometimes iodide, iodate and perchlorate. The methods are in general similar to those for potassium nitrate. Sodium nitrate is now largely made from synthetic nitric acid. This gives a comparatively pure product, which may, however, contain small quantities of nitrite, chloride and soda. The nitrite may be tested for in small quantities by potassium iodide and starch, the estimation being made colorimetrically. Larger quantities may be estimated by titration with potassium permanganate.

(c) Ammonium Nitrate

Mol. wt., 80·05; sp. gr., 1·725; M.P., 169·6°; decomp. at about 200°; soluble in 100 parts water, 118 at 0°, 870 at 100°; slightly soluble in alcohol.

This salt is used very extensively in explosives. Owing to a number of disasters with ammonium nitrate explosives (*e.g.* Oppau) a great

[1] *Amer. Chem. J.*, 1903, **32**, 242. [2] *U.S. Bur. Mines, Bull.* **51**, 1913, 70.
[3] Busch, *Ber.*, 1905, **38**, 861; cf. *U.S. Bur. Mines, Bull.* **96**, 1913, 60; *cf.* also Vol. I., p. 473.

amount of research has been carried out on the use of this substance alone and in mixtures for explosive use. The material should be white or very slightly grey or yellowish. It should give a clear solution in water. The size of particles is generally specified. The moisture is estimated by drying in a vacuum over sulphuric acid for at least twenty-four hours ; if it is necessary to shorten the time by warming, the temperature should not exceed 70°.

Oils are sometimes present, being added to reduce the hygroscopicity. These may be estimated by extraction with ether or benzene. Nitrite should be absent, and there should be practically no acidity to methyl orange.

Pyridine and thiocyanate may be present in ammonium nitrate made from gas-works ammonia and should be avoided as far as possible.[1] Methods for the estimation of pyridine are given by Ladd [2] and by Harvey and Sparks.[3] Thiocyanate is estimated colorimetrically. Ammonium nitrate made from sodium nitrate by double decomposition practically always contains sodium salts. The total ammonium nitrate content is determined by estimations of the ammonia and nitrate by the usual methods.

(d) Barium Nitrate

Mol. wt., 261·4; sp. gr., 3·23; M.P., 592°; soluble in 100 parts water, 5·0 at 0°, 34·2 at 100°.

Barium nitrate is used in certain explosives such as tonite, and in firework mixtures. It is tested for moisture, insoluble matter, neutrality, chloride, chlorate, sodium, calcium, and lead. On addition of slight excess of sulphuric acid and filtering, the solution should give only traces of residue after evaporation and ignition. The total barium is estimated by the usual methods. The nitrate is best estimated by reduction to ammonia. Barium nitrate may be readily estimated in mixed explosives by extraction with water and precipitation with sulphuric acid.

(e) Lead Nitrate

Mol. wt., 331·2; sp. gr., 4·41 ; decomp. at about 200°; soluble in 100 parts water, 36·5 at 0°, 127 at 100°; slightly soluble in alcohol.

Lead nitrate should dissolve in water without residue. On adding sulphuric acid, and filtering, the liquid should give practically no residue on evaporation and heating. Impurities are tested for as in barium nitrate.

[1] Robertson, *J. Chem. Soc.*, 1921, **119**, 27.
[2] *Ind. Eng. Chem.*, 1919, **11**, 552.
[3] *J. Soc. Chem. Ind.*, 1918, **37**, 41 T.

II. Chlorates and Perchlorates

(a) Potassium Chlorate

Mol. wt., 122·55 ; sp. gr., 2·34 ; M.P., 370° ; decomp. slightly above M.P. ; soluble in 100 parts water, 3·3 at 0°, 56 at 100° ; slightly soluble in alcohol.

Potassium chlorate should be pure white, free from smell and in a very fine crystalline condition. The degree of fineness is usually specified. The purity of the salt is important for explosive purposes, as impurities may lead to increased sensitiveness to shock and friction. The moisture is usually restricted to 0·2 to 0·5 per cent.

The aqueous solution should be neutral, and should give only traces of insoluble matter ; gritty matter such as sand is particularly to be avoided. The potassium chlorate should be practically free from chloride, perchlorate, nitrate, sulphate, carbonate and lead. Sodium, calcium and arsenic are sometimes tested for. Organic matter should be absent.

Bromate frequently occurs in appreciable proportions up to 0·5 per cent. and is to be avoided. It gives a blue colour with potassium iodide and starch in presence of dilute sulphuric acid ; chlorite and hypochlorite also react with starch iodide. Chlorate gives a similar coloration on longer standing. Other qualitative tests are given by Dimitroff,[1] Monnier,[2] and Nicola.[3] The bromate may be estimated quantitatively by addition of potassium iodide and dilute acid, and titrating back the free iodine with thiosulphate. Specification limits vary from 0·05 to 0·15 per cent.

Nitrates may be tested for by evaporating with a solution of brucine and oxalic acid in alcohol ; the presence of nitrate is indicated by a red colour.

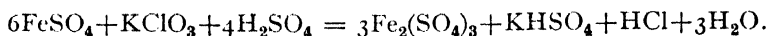
Perchlorate is detected by addition of a 0·3 per cent. solution of methylene blue, which gives a violet precipitate with green fluorescence.[4]

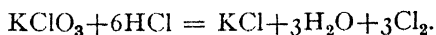
Estimation of Chlorate. The total chlorate may be estimated as follows, and should be at least 98·5 to 99 per cent.

(*a*) By ferrous sulphate. The chlorate solution is placed in a flask fitted with a Bunsen valve. A solution of 100 g. ferrous sulphate crystals and 100 ml. conc. sulphuric acid in a litre of water is prepared, and 25 ml. of this is added to the flask and boiled for ten minutes. After cooling, the excess of ferrous salt is titrated back with *N*/2 permanganate. It is desirable to add some manganous sulphate, as the hydrochloric acid formed may otherwise give rise to difficulty.

[1] *Z. anal. Chem.*, 1923, **62**, 453.
[2] *Ann. Chim. analyt.*, 1916, **20**, 237.
[3] *Giorn. farm. Chim.*, 1912, **61**, 538.
[4] Monnier, *Ann. Chim. anal.*, 1917, **22**, 1.

It is also recommended to titrate slowly. The reaction which takes place is as follows :—

$$6FeSO_4+KClO_3+4H_2SO_4 = 3Fe_2(SO_4)_3+KHSO_4+HCl+3H_2O.$$

(*b*) Iodometric method.[1] The chlorate is heated with excess of hydrochloric acid, and the gas evolved is passed into excess of potassium iodide solution. The reaction is as follows :—

$$KClO_3+6HCl = KCl+3H_2O+3Cl_2.$$

The chlorine exists partly as lower oxides, but this does not affect the amount of iodine liberated. The chlorate is weighed and placed in a flask. Fuming hydrochloric acid is added, and the flask is quickly connected to the tube passing to the potassium iodide solution (1 : 10). After boiling off the chlorine, an excess of $N/10$ thiosulphate is added to the iodide solution and titrated back with iodine solution, using starch as indicator.

Other methods depend upon reduction of the chlorate with sulphurous acid, iron,[2] etc., and estimation of the chloride formed, and upon precipitation as nitron chlorate.[3] Methods for the detection of small quantities of chlorate have been given under potassium nitrate.

(b) Sodium Chlorate

Mol. wt., 106·45 ; sp. gr., 2·49 ; M.P., 248° ; soluble in 100 parts water, 82 at 0°, 204 at 100° ; soluble in alcohol.

Sodium chlorate is deliquescent and is relatively little used. It may be tested in the same way as potassium chlorate. Roman [4] gives the following specification : sodium chlorate 99·5 per cent., sodium chloride 0·2, bromide 0·1 ; traces of heavy metals and alkaline earths ; no mechanical impurities ; no insoluble residue in water.

(c) Potassium Perchlorate

Mol. wt., 138·55 ; sp. gr., 2·52 ; M.P., 610° ; soluble in 100 parts water, 0·7 at 0°, 18·7 at 100°.

Potassium perchlorate forms a white, crystalline solid, which is very sparingly soluble in water. It is not hygroscopic. It should be in a fine state of subdivision. It is much more stable than the chlorate ; it is not readily decomposed by acids, and is reduced with difficulty in solution. It should be free from sodium salts.

Chlorides and sulphates should be present only in small proportion. Chlorate should be present only in traces. This may be tested

[1] *Cf.* Rupp, *Z. anal. Chem.*, 1918, **57**, 226.
[2] Hendrixson, *Amer. Chem. J.*, 1903, **32**, 242.
[3] Hes, *Z. anal. Chem.*, 1909, **48**, 81.
[4] *Nitrocellulose*, 1932, **3**, 162.

for qualitatively by warming with hydrochloric acid. A smell of chlorine indicates the presence of chlorate. The chlorate may be estimated colorimetrically by the yellow-brown colour produced on warming with hydrochloric acid and potassium iodide.

Potassium perchlorate may be detected in mixtures by the methylene blue reaction (see under Potassium Chlorate). It may be estimated quantitatively by heating, as described under Potassium Nitrate, or by nitron[1]; also by precipitation as methylene blue perchlorate and titration of the excess of methylene blue with picric acid.[2] It can also be reduced with titanous sulphate or chloride.[3]

Sodium perchlorate contains a higher proportion of oxygen, but is not suitable for use on account of its hygroscopicity.

(d) Ammonium Perchlorate

Mol. wt., 117·50; sp. gr., 1·87; soluble in 100 parts water, 12·4 at 0°, 88·2 at 100°; slightly soluble in alcohol and acetone.

The examination is similar to that of the potassium salt. Absence of chlorate is of special importance. Chlorides and sulphates should not exceed about 0·5 per cent., ash 0·5 per cent., and moisture 0·25 per cent. The ammonium perchlorate content should be at least 99 per cent.

III. Ingredients of Gun-powder

(a) Potassium Nitrate (see p. 489).

(b) Sulphur[4]

At. wt., 32·06; sp. gr., 2·06 (rhombic); melts at 112-119°; boils at 444·5°; insoluble in water; soluble in many organic solvents, especially carbon disulphide (100 parts dissolve 37 parts sulphur at 15°).

For explosive purposes finely powdered roll sulphur is used. It must be free from acid. The moisture is estimated by drying in a vacuum or by warming, but a temperature of 70° should not be exceeded. The loss of weight should not be more than 1 per cent. The residue on burning off the sulphur should not exceed 0·15 per cent. Some specifications permit up to 0·5 per cent. The residue should be free from sand.

Arsenic is indicated by a bright yellow or reddish colour, and may be estimated by warming 5 g. of sulphur with 100 ml. ammonia to 50°–60° for fifteen minutes, filtering, acidifying the liquor, and treating

[1] Busch, *Ber.*, 1905, **38**, 861; *U.S. Bur. Mines, Bull.* **96**, 65.
[2] Bolliger, *Z. anal. Chem.*, 1933, **94**, 403.
[3] *Z. ges. Schiess- u. Sprengstoffw.*, 1920, **15**, 56.
[4] *Cf.* Vol. I., p. 358.

with hydrogen sulphide. There should be no weighable precipitate. Alternatively, a titration method with silver nitrate and potassium chromate may be used.[1] The Gutzeit test for arsenic may also be employed.

Sulphur may be extracted from mixtures by freshly distilled carbon disulphide. It may be determined by evaporating at least three times with strong *aqua regia* to convert it to sulphuric acid, and precipitating with barium chloride.

(c) Charcoal

The examination is mainly physical. Good charcoal should have a deep black, velvety fracture, low density, and should be soft and easily rubbed to powder. It should not scratch copper and should ring well when struck. Charcoal from different woods may be recognised by the pith, which is round and brown for dogwood, black and round for willow, triangular for alder, and small, round and black for hazel wood. Birch and poplar are also sometimes used. Brown charcoal is recognized by its colour. The moisture is estimated by heating at 100° and should not exceed 4 per cent. The carbon content is sometimes determined, and ranges from about 70 to 75 per cent. The ash is determined in the usual way. It should not contain gritty matter.

IV. Various Ingredients

(a) Graphite

Graphite is used for coating powders. It must give an adherent, uniform coating and for this purpose must be very finely ground. It should have a uniform grey colour, and a smooth feel when rubbed. Pure graphite has a specific gravity of 2·255. It should be free from acid. The ash is determined in the usual way, but vigorous heating is necessary to burn off the graphite. The residue may amount to 15-25 per cent. Silicates should be absent. Volatile matter is estimated by heating in an atmosphere of nitrogen. The carbon content may be estimated by combustion in a current of oxygen, and determination of the carbon dioxide. Sulphur is determined by heating with magnesia and sodium carbonate, then with ammonium nitrate or sodium peroxide to convert to sulphate, which is estimated as barium sulphate.

(b) Aluminium

At. wt., 26·97; sp. gr., 2·70; M.P., 658°.

Aluminium is used in a finely powdered condition or as flake in explosive mixtures. The degree of fineness and bulk density are

[1] Schäppi, *Chem. Ind.*, 1881, 4, 409.

usually specified. The aluminium must be as free as possible from oxide and from impurities which promote oxidation on storage. The specification limits for aluminium content range from about 92 to 98 per cent. Iron is frequently present up to 0·5 or 1 per cent., and small quantities of zinc and copper are met with (0·1 to 0·2 per cent.). The copper content should be as low as possible, since larger amounts make the aluminium very reactive towards nitrates. Silicon is also found up to about 0·5 per cent. Oily matter is often present up to 0·3–0·5 per cent. Soap should not be present in more than very small proportions. The loss of weight on heating to 100° for an hour should not exceed 0·25 per cent. For the determination of the aluminium content, the metal is dissolved in hydrochloric acid or potassium hydroxide solution, and the hydrogen evolved is measured, or determined by a gravimetric method.[1] Other methods depend upon reduction of ferric sulphate, and on conversion of the aluminium to chloride which is then distilled off in a current of hydrogen chloride.[2]

(c) Magnesium

At. wt., 24·32 ; sp. gr., 1·74 ; M.P., 650°.

Magnesium is used in a powdered form. The degree of fineness is usually specified. The magnesium should be as free as possible from oxide and from other metals. Small quantities of iron are usually present (0·5 to 1 per cent.). Copper, aluminium, manganese, zinc, lead, calcium and silicon may be present in traces. Gritty matter is to be avoided, and oil or fat should be present only in traces. The content of metallic magnesium is estimated by measuring the hydrogen evolved on treatment with hydrochloric acid (*cf.* aluminium). Methods for the testing of magnesium are given by Guerin.[3]

(d) Paraffin Wax

This should be white and as transparent as possible. It should have no taste or smell. It must be free from mechanical impurities and acidity, and must dissolve completely in acetone or carbon disulphide. On ignition it should give very little ash. The melting point is not very definite. It is generally specified for the special purpose for which the paraffin wax is required. The determination of the setting point is sometimes preferred. The " dropping point " of

[1] Nicolardot, *Bull. Soc. Chim.*, 1912 (4), **11**, 406 ; *Chim. et Ind.*, 1919, **2**, 641 ; Wogrinz, *Z. ges. Schiess- u. Sprengstoffw.*, 1919, **14**, 64 ; Beyne, *Ann. Chim. anal.*, 1921 (2), **3**, 360 ; Capps, *Ind. Eng. Chem.*, 1921, **13**, 808 ; 1922, **14**, 81.

[2] Kohn-Abrest, *Bull. Soc. Chim.*, 1904 (3), **31**, 232 ; 1909 (4), **5**, 207, 768 ; Jander and Wendehorst, *Z. angew. Chem.*, 1922, **35**, 244.

[3] *Ann. Chim. anal.*, 1926, II., **8**, 34.

Ubbelohde[1] is also much used. The apparatus for this test consists of a thermometer of suitable range and a small glass cup with a hole in the bottom. About 0·2 g. of the paraffin or mineral jelly is placed in the cup, which is then fitted on to the bottom of the thermometer bulb. On slowly heating the thermometer and cup, the temperature at which drops of melted paraffin fall away from the cup is noted.

(e) Colophony

This is a brittle, vitreous material of yellow to brown colour and sp. gr. 1·07 to 1·08. It has very little taste or smell. It is insoluble in water, but dissolves in alcohol and most other organic solvents. It has a very indefinite melting point. On heating it softens at 70° and becomes molten at about 108°. It should not lose more than 0·2 per cent. on heating at 100°.

(f) Castor Oil

Castor oil is used to reduce the sensitiveness to friction. It is also a waterproofing agent and prevents the recrystallization of potassium chlorate. The oil is colourless or pale yellow, highly viscous, and somewhat lighter than water (sp. gr. 0·96 to 0·97 at 15°). It is optically active and has a refractive index of 1·4773. It is miscible with absolute alcohol and many other organic solvents, but is insoluble in petroleum-ether and benzine, and incompletely soluble in 90 per cent. alcohol. A mixture of 10 ml. of the oil and 50 ml. of alcohol of sp. gr. 0·829 at 17·5° should give no turbidity. On shaking with an equal volume of 50 per cent. nitric acid it should not blacken. The acidity is determined by dissolving in alcohol and titrating with alkali. The saponification number is estimated in the usual way. Colophony can be detected by dissolving in acetic anhydride and adding a drop of concentrated sulphuric acid (violet or red colour). Paraffin wax may be detected by saponifying 5 g. of the oil with 20 ml. of a solution of 40 g. sodium hydroxide in 93 ml. water and 500 ml. glycerol. The hot liquid is then added drop by drop to 50 ml. of methyl alcohol. In absence of paraffin wax the liquid remains clear on cooling; 2 per cent. of wax causes the liquid to become cloudy, and after a time gelatinous. The refractive index and viscosity are also made use of to ensure absence of impurities.

(g) Kieselguhr

Kieselguhr is used for the manufacture of dynamite. It consists of diatoms which are capable of absorbing considerable quantities of nitroglycerine or other liquids. It is obtainable commercially in

[1] *Z. angew. Chem.*, 1905, **18**, 1220; Reilly and Rae, *Physico-Chemical Methods*, 1940.

fairly pure condition, but is subjected to calcination at the dynamite factory before mixing with the nitroglycerine. It should be white or faintly reddish and should have a smooth feel when rubbed between the fingers. It should be as free as possible from sand, acid, and organic matter. The water content should not exceed 1 per cent. Sand may be separated by shaking with water and allowing to settle quickly. The separation is facilitated if the kieselguhr is first broken down by boiling with strong alkali. The absorptive capacity is ascertained by mixing weighed quantities of nitroglycerine and kieselguhr, filling into a cavity in a wooden block and pressing with a wooden plunger by means of a definite weight. The lower end of the cavity is open and is covered with a piece of parchment paper. The amount of nitroglycerine which is pressed out is an inverse measure of the absorptive capacity. A rough indication is also given by the amount of nitroglycerine necessary to make the kieselguhr appear wet ; a good kieselguhr should take up at least four parts.

(h) Wood Meal

Wood meal should be free from acid and foreign substances, especially sand and metallic particles. No chemicals should be used in the manufacture, and bleaching agents should be avoided. The degree of fineness is generally specified. Larger fragments of wood should not be present.

Limits for the moisture content range from 5 to 10 per cent. The ash should not exceed 0·5 to 1·0 per cent. Resin is determined by extraction with ether. Extraction with alcohol removes tannin, etc. These extracts should be very small in quantity. Wood meal contains small quantities of water-soluble matter, which should be taken into account in the estimation of wood meal in dynamite, etc.

The cellulose content may be estimated by treatment with caustic soda and chlorine.[1]

Wood meal should absorb liquids readily. Thus it should retain 60 to 70 per cent. of nitroglycerine without exudation. The combustibility is tested by mixing 1 part of wood meal with 3 parts of potassium nitrate and burning in a lightly covered crucible. The residue should not exceed 10 per cent. The rapidity of burning is measured by filling some of the mixture into a groove in a sheet of metal and igniting at one end.

The bulk density is measured by adding the wood meal little by little to a 100 ml. measuring cylinder, which is knocked on the table after each addition to shake the wood meal down. The quantity which fills 100 ml. is weighed.

[1] Cross and Bevan, *J. Chem. Soc.*, 1889, **55**, 199 ; *cf.* Renker, *Z. angew. Chem.*, 1910, **23**, 193.

Wood meal may be detected in mixtures by the microscope or by the phloroglucinol test. 1 gram of phloroglucinol is dissolved in 15 ml. of alcohol, and 10 ml. of syrupy phosphoric acid is added. A little of the meal is rubbed with 0·5 ml. of this reagent in a porcelain dish. Wood fibres show a rose colour changing to carmine. Apart from wood meal other forms of meal (corn, potato) are similarly used.

(i) Chlorides, Oxalates, Carbonates

Sodium and potassium chlorides are much used in industrial explosives. They are generally obtainable in a sufficiently pure condition. They should be free from hygroscopic impurities. The degree of fineness is of importance and is generally specified ; large particles should not be present.

The oxalates of potassium, sodium, and ammonium should be pure white, and free from mechanical impurities. The two former should be free from acidity and alkalinity ; ammonium oxalate may develop slight acidity by hydrolysis and the litmus paper tends to change colour on drying. The sodium salt is anhydrous, the two others have water of crystallization. They should dissolve practically completely in water and should be free from chlorides, sulphates and heavy metals. The ammonium salt should leave no residue on ignition. Oxalates are readily detected as the calcium salt and the purity can be determined by titration with permanganate.

Sodium carbonate is occasionally used as a stabiliser in blasting explosives. It should be of 98 to 99 per cent. purity, and should contain only traces of chlorides, sulphates, and ammonia. It should dissolve in water without residue.

Sodium bicarbonate should be finely powdered, and should dissolve completely in water. Carbonates of other metals should be present only in traces, and chlorides and sulphates should also be practically absent. The purity should be at least 99 per cent.

Calcium carbonate should be in a very finely dissolved condition ; the state of subdivision is usually specified. It should be practically free from calcium oxide or hydroxide and from salts of metals other than calcium.

(j) Cuprene

For gun-powder required for burning under reduced pressure, Grimwood[1] recommends the use of cuprene, a polymerised product from acetylene. This may be used to replace either wholly or in part the charcoal of gun-powder. Even at very low pressures the rates of burning are not appreciably altered when this substance is used.

[1] B.P. 283741.

V. Stabilisers

(a) Camphor

$C_{10}H_{16}O$; mol. wt., 152·2 ; sp. gr., 0·985 at 18° ; M.P., 180° ; B.P., 209° ; soluble in water 0·1 per cent. ; soluble in organic solvents.

Apart from natural camphor, the synthetic material is now made in considerable quantities. Natural camphor is optically active, the synthetic product is the racemic form, and is inactive except for small quantities of impurities.

On heating, camphor should not begin to sinter below 173° and should not melt below 175°. On sublimation it should leave practically no residue (0·1 per cent.). It is tested for acid by dissolving in alcohol, precipitating with water and testing the solution. The presence of water is indicated by turbidity on dissolving in petroleum ether. Camphor gives a yellow to brown solution in concentrated sulphuric acid, according to the organic impurities present.

Crane and Joyce[1] recommend for the determination of the purity of camphor—

(1) Determination of residue on sublimation.
(2) Sp. gr. of a 10 per cent. solution in benzene.
(3) Optical rotation (for natural camphor).

Désmaroux[2] gives a method for the determination of camphor in presence of nitroglycerine and diphenylamine.

(b) Diphenylamine

$(C_6H_5)_2NH$; mol. wt., 169·2 ; sp. gr., 1·159 ; M.P., 54° ; B.P., 302° ; practically insoluble in water ; soluble in most organic solvents.

The compound should be white or pale yellow. It should melt at 52° to 54° and should yield practically no insoluble residue in ether or alcohol. It should also give a clear solution in pure sulphuric acid (a blue colour indicates the presence of nitrate). It should have no unpleasant smell. Aniline bases should be present only in traces (0·001 per cent.). These may be tested for by bleaching powder.

In the detection of diphenylamine the nitric acid reaction is used. The quantitative estimation is described under Smokeless Powder (p. 541).

(c) Substituted Ureas

Symmetrical diethyl- and dimethyldiphenyl-urea are known as Centralite I and II respectively. They are used as stabilisers, as they absorb the oxides of nitrogen, formed by the decomposition of nitric esters.

[1] *J. Soc. Chem. Ind.*, 1907, **26**, 386. [2] *Mém. Poudres*, 1928, **23**, 43.

Centralite I melts at 72° and Centralite II at 121·5°. They sublime above the melting point. They are very sparingly soluble in water, but dissolve readily in alcohol and ether. They should be almost colourless and free from aniline, volatile substances, chlorides, and mechanical impurities. They should give clear solutions in alcohol and should give no residue on incineration.

Asymmetric diphenylurea (acardite) also belongs to this class of compounds. It melts at 189°. On boiling with sodium hydroxide solution it is hydrolysed to diphenylamine which can be driven over by steam. The symmetrical derivative melts at 235°. It is not volatile in steam.

Substituted urethanes are also used as stabilisers.

The estimation of centralite, etc., is dealt with under Smokeless Powders (p. 541).

(d) Mineral Jelly

This is used principally for the manufacture of cordite. It should be free from foreign matter, scales and particles, and should have a flash point of at least 400° F. (205° C.) and a sp. gr. of not less than 0·87 at 100° F. (37·8° C.). It should not lose more than 0·2 per cent. in weight on heating for 12 hours on a water-bath and should be practically free from mineral matter. The acidity may be tested by dissolving in ether, allowing to settle and titrating a measured portion of the liquid with alcoholic potassium hydroxide. The mineral jelly should be practically neutral. Mineral jelly has no definite melting point, but the dropping point may be determined by Ubbelohde's method[1] (p. 9). It is important that the mineral jelly shall not have been melted for two or three days before testing.

Mineral jelly is practically insoluble in a mixture of 4 parts methyl alcohol and 1 part water, and this is made use of in the separation of mineral jelly from nitroglycerine, etc.

Camphor, substituted ureas and triphenyl phosphate[2] are sometimes used to modify the rate of burning of gun-powder. Phthalides are claimed to have advantages over centralite in certain smokeless powders.[3]

VI. Nitration Acids

(a) Nitric Acid

The methods of testing are given in Vol. I., p. 489. These include the total acidity, lower oxides of nitrogen, sulphuric acid, chlorine, iodine and mineral matter. The lower oxides are usually restricted

[1] *Z. angew. Chem.*, 1905, 18, 1220; Reilly and Rae, *Physico-Chemical Methods*, 1940.
[2] Oslen, U.S. P. 1748455.
[3] Parodi, *Cong. intern. quim. pura applicada*, 1934, 4, 447.

to 1 per cent. (as NO_2). Chlorine should not exceed 0·03 per cent. and mineral matter 0·01 per cent. Nitric acid may contain traces of tetranitromethane and of chloronitromethanes, which are liable to find their way into nitroglycerine and lower the heat test.[1]

(b) Sulphuric Acid and Oleum

Methods of testing are given in Vol. I., pp. 416, 456.

(c) Mixed Acids and Spent Acids [2]

Mixed acids for nitroglycerine manufacture should be as free as possible from suspended matter, such as sulphates of iron or lead, as these may delay the separation.

A resumé of the methods of testing of nitration acids for explosives manufacture is given by Schmandt.[3]

In the spent acids the nitric acid content is lower and the water content higher than in fresh mixed acids. They also contain organic matter which differs according as the acids are from nitrocellulose, nitroglycerine, or nitroaromatic compounds. The presence of these and of muddy suspensions gives rise to some difficulties in analysis. In the determination of nitrogen by the nitrometer method allowance must be made for dissolved nitroglycerine; this may be determined by extraction with ether or chloroform and evaporating gently. The estimation of nitrous acid may also be affected by organic matter. Raschig [4] avoids this by adding potassium iodide and titrating the liberated iodine in an atmosphere of carbon dioxide.

Webb [5] gives the following method for the waste acid from nitroglycerine manufacture: A sample is maintained at 120° in a calcium chloride bath for 20 minutes, and the nitric acid is driven off by a current of steam. The residual solution contains sulphuric and oxalic acid. The latter is estimated by titration with permanganate at 60° and the sulphuric acid is determined by titration with alkali and methyl red after addition of 1 ml. of 3 per cent. hydrogen peroxide for each 5 ml. of permanganate previously used up. This is to destroy organic matter. It is necessary to calculate from the permanganate titration the amount of sulphuric acid which is used up in the reaction between permanganate and oxalic acid and to add this to the sulphuric acid estimated by the alkali titration. The nitric acid is determined by Lunge's method. Dissolved nitroglycerine is oxidised by potassium bichromate, and the excess of bichromate estimated by potassium iodide and thiosulphate.

[1] Crawford, *J. Soc. Chem. Ind.*, 1922, **41**, 321 T.
[2] *Cf.* Vol. I., p. 497.
[3] *Nitrocellulose*, 1932, **3**, 219; 1933, **4**, 23.
[4] *Ber.*, 1905, **38**, 3911.
[5] *J. S. African Chem. Inst.*, 1927, **10**, 13.

VII. Cellulose

(a) Cotton Cellulose

The cotton cellulose used for the manufacture of nitrocellulose must be as free as possible from husks, seeds, paper, dust, coal, sand, woven and twisted masses, and must not contain residues of soda or bleach. It should not be acid. The moisture is determined by heating 5 g. at 103° to 105° to constant weight and may amount to 7 to 8 per cent. The ash should not exceed 0·5 to 1 per cent. Oily matter is determined by extraction with ether and is generally restricted to 0·4 to 0·6 per cent. Starch should be absent or present only in traces.

Alpha-cellulose.[1] 10 g. of cellulose is broken down by kneading in a mortar with 50 ml. of 17·5 per cent. sodium hydroxide solution free from carbonate. After 30 minutes 50 ml. of water is added, and the cellulose is filtered and washed. The mass is wetted with hot dilute acetic acid, again washed, and dried. The residue represents the alpha-cellulose, after deducting the weight of the ash.

Reducing Substances. These are tested for by the " copper value." In the method of Schwalbe [2] the cotton is boiled with Fehling's solution, prepared by adding copper sulphate solution to alkaline Rochelle salt. In Braidy's modification, which is stated to give more consistent results,[3] 2·5 g. of very finely divided air-dry cotton is treated with a mixture of 5 ml. of 10 per cent. copper sulphate (cryst.) and 95 ml. of an almost saturated solution of sodium carbonate and bicarbonate (350 g. soda crystals and 50 g. bicarbonate made up to 1 litre). The cotton is immersed by means of a rod and the air bubbles are allowed to escape; the flask is then surrounded with boiling water for exactly three hours. The contents are filtered off on an asbestos filter and washed first with dilute sodium carbonate solution and then with water. Then the residual cuprous oxide is dissolved by treatment with a solution containing 100 g. of iron alum and 140 g. of concentrated sulphuric acid per litre. Two such treatments usually suffice. The filter is then washed with 2 *N*-sulphuric acid; the combined filtrate and washings are titrated with *N*/25 potassium permanganate solution. According to Brissaud [4] the test is affected by air. Examples of copper values of different celluloses are given by Marshall.[5]

[1] *Cf.* Gabillion, *Rev. Chim. Ind.*, 1935, **44**, 313.
[2] *Ber.*, 1907, **40**, 1347, 4523; *J. Soc. Chem. Ind.*, 1907, **26**, 548.
[3] *Rev. Gén. Mat. Col.*, 1921, **25**, 35; *cf.* Koehler and Marqueyrol, *Mém. Poudres*, 1921, **18**, 73; Clibbens and Geake, *J. Text. Inst.*, 1924, **15**, T. 27; Heyes, *J. Soc. Chem. Ind.*, 1928, **47**, 90 T.
[4] *Mém. Poudres*, 1932-3, **25**, 244.
[5] Marshall, *Explosives*, vol. ii., 1917, p. 692.

Alkali-soluble Substances. The methods vary somewhat in detail. The following conditions are given by Landon.[1] 5 g. of dried cellulose is placed in a litre flask, and 300 ml. of 10 per cent. potassium hydroxide solution (or the equivalent of sodium hydroxide) added. The hydroxides should be free from carbonate. The mixture is boiled under a reflux condenser for three hours. The ebullition should be as regular as possible; fragments of porcelain may be added to prevent bumping, and should be removed afterwards. The mixture is poured into a litre of cold water; the flask is rinsed carefully and acetic acid is added to destroy combinations of cellulose and alkali. The cellulose is filtered, washed with hot water and dried. The loss of weight represents the alkali-soluble material. Landon gives a limit of 3 per cent. Part of the alkali-soluble material can be reprecipitated with acid. This is known as wood gum. The following method is in use: 15 g. of the dried cellulose is immersed in 300 ml. of a 5 per cent. solution of sodium hydroxide, and allowed to stand for twenty-four hours at 18° to 20° with frequent shaking. The liquid is filtered off and 100 ml. mixed with 200 ml. of alcohol (92·5 per cent. by weight). A little phenolphthalein is added and then 9·5 ml. of hydrochloric acid (1·19) to neutralize most of the alkali. The neutralization is completed with normal acid, and a further 5 ml. of acid is added. After twenty-four hours the precipitate is collected on a tared filter paper or in a Gooch crucible, washed with alcohol and ether, dried at 100° and weighed.

Cotton is also tested for ligneous matter by absorption of dyes (fuchsine, methylene blue, malachite green)[2] and for the viscosity of its solution in cuprammonium liquor.[3] Gabillion gives the following figures for various cottons:—

Moisture, 4·5 to 6·0; ash, 0·1 to 0·25; fats, 0·1 to 0·25 (maximum) 0·8; iron, 0·008; insoluble in H_2SO_4, 0·1 to 0·5; alpha-cellulose, 99 per cent.; copper number (unbleached) 0·07 to 0·10, (moderately bleached) 0·1 to 0·2, (strongly bleached) 3 to 4; potash number, 2.

(b) Wood Cellulose[4]

Wood cellulose which is to be converted to nitro-cellulose must be in a form in which it can be readily dipped into the nitration acids

[1] *Mém. Poudres*, 1932-3, **25**, 455.

[2] Barrett, *J. Soc. Chem. Ind.*, 1920, **39**, 81 T.

[3] Gibson and Jacobs, *J. Chem. Soc.*, 1920, **117**, 473; Gibson, Spencer and McCall, *ibid.*, 1920, **117**, 479; Joyner, *ibid.*, 1922, **121**, 1511, 2395; *R.D. Report* No. 22, Pt. III., 1923 (H.M.S.O.); Gabillion, *Rev. Chim. Ind.*, 1935, **44**, 330.

[4] Compare Dorée, *The Methods of Cellulose Chemistry*; Schorger, *Chemistry of Cellulose and Wood*; Schwalbe, *Die Chemie der Cellulose*, also *Z. angew. Chem.*, 1918, **31**, i. 50; *Z. ges. Schiess- u. Sprengstoffw.*, 1920, **15**, 17, 38, 53, 91; Scharrnbeck, *ibid.*, 1934, **29**, 33, 67, 98, 133, 196, 230, 266; Gabillion, *Rev. Chim. Ind.*, 1935, **44**, 310, 330.

and must be highly absorbent to permit of the penetration of the acids. It should be practically free from acidity and alkalinity, and from any residual chlorine from the bleaching process.

The moisture is estimated by heating 5 g. of the cellulose to 103° to 105° to constant weight. It is desirable to dry the cellulose partially at a lower temperature, otherwise some charring may take place at 105°. The dried cellulose should be allowed to cool in a stoppered weighing bottle, as it reabsorbs moisture very readily. Limits of 6 to 8 per cent. are specified.

The ash is determined in the usual way, taking 5 to 20 g. of material and finishing at a dull red heat. If calcium sulphate is present in quantity, it may be reduced ; in this case the cellulose may be first destroyed with nitric acid.

Fats and resins are determined by extraction with ether. Figures up to about 1 per cent. are given. Extraction with alcohol is sometimes also included. The method of determination of alpha-cellulose is given under Cotton (p. 504). Alkali dissolves xylan together with some oxycellulose, etc., and on neutralization a mixture of substances is precipitated which is designated as wood gum. The method of estimation is given under Cotton Cellulose (p. 504). The figure obtained on neutralization is known as the neutral wood gum number. Excess of acid gives a somewhat lower figure (acid wood gum). Figures of 5 to 8 per cent. are given for the neutral wood gum. It is to be observed that the precipitate readily carries down a considerable proportion of sodium chloride from solution ; this should be estimated and deducted from the total.

Pentosans are estimated by conversion to furfural. This is effected by distillation with dilute hydrochloric acid. Oxycellulose and other constituents of wood cellulose are also stated to yield small quantities of furfural. Methyl pentosans similarly yield methyl furfural. The wood cellulose is distilled with 12 per cent. hydrochloric acid until no more furfural is evolved. The furfural is then determined by precipitation with phloroglucinol. This gives a phloroglucide which can be washed, dried, and weighed.[1]

According to Heuser and Boedeker, furfural = (phloroglucide + 0·001) × 0·571, and pentosan = furfural × 1·375.

A more expeditious volumetric method is given by Powell and Whittaker.[2] 0·5 to 0·8 g. of material is distilled with 12 per cent. hydrochloric acid until the distillate gives no more pink colour with aniline acetate. The apparatus used for the distillation should have all-glass connections. Into each of four well-stoppered bottles is

[1] *Cf.* Lenze, Pleus, and Müller, *J. prakt. Chem.*, 1920, **101**, 242 ; Heuser and Boedeker, *Z. angew. Chem.*, 1921, **34**, 462.

[2] *J. Soc. Chem. Ind.*, 1924, **43**, 35 T.

pipetted 25 ml. of standard sodium bromide-bromate (approx. $N/10$). To two of the bottles are added 200 ml. of the above distillate, and to the others 200 ml. of 12 per cent. hydrochloric acid. After standing for an hour in the dark, about 10 ml. of 10 per cent. potassium iodide solution is added, and the iodine is titrated with $N/10$ thiosulphate. The difference between the blank and the test titration is a measure of the furfural. 1 g. mol. furfural is found to react with 4·05 g. atoms of bromine. According to Schwalbe,[1] Kraftcellulose gives the highest pentosan content (7·6 to 9·3 per cent.); next comes unbleached soda cellulose with 5·9 to 7·7 per cent. Sulphite cellulose gives 3·3 to 4·6 per cent.

The copper value is used for the estimation of reducing substances (mainly oxycellulose). The method is given under Cotton Cellulose (p. 504). It is stated that pentosans and other constituents of wood cellulose also react to some extent. Hydrocellulose is formed by the action of acids on cellulose. On further hydrolysis with acid and neutralization, it reduces Fehling's solution. Estimations of the hydrocellulose are not usually included.

Lignin presents considerable difficulties, as the constitution is unknown and definite quantitative reactions are not available. It contains hydroxy, acetyl, and methoxy groups. It can be acetylated and nitrated. Numerous colour reactions have been suggested. The commonest of these is the phloroglucinol reaction. A solution of 1 g. phloroglucinol in 50 ml. alcohol is mixed with 25 ml. conc. hydrochloric acid. This gives a red colour with lignin. It is important that the solutions be freshly mixed. It is sometimes specified that the cellulose shall not give more than a faint rose colour. Another test in common use is to dissolve 0·02 g. wood cellulose in 5 ml. of conc. sulphuric acid and allow to stand for an hour. This gives a brown colour. Results of these and numerous other colour tests are given by Schwalbe,[2] but all of the methods are open to criticism. The determination of the methoxy-group by the Zeisel method is sometimes used as a quantitative test, but the reaction is also given by methyl pentosans.

The wood cellulose may also be examined for viscosity in cuprammonium solution.[3] To ascertain whether wood cellulose absorbs nitration acids readily, about 1 g. is pressed together lightly by hand and thrown on to a mixed acid containing 20 to 25 per cent. nitric, 70 to 60 per cent. sulphuric and 10 to 15 per cent. water. The cellulose should sink within one minute. On nitration it should neither become pappy nor become stiff through parchmentising. The following limits

[1] *Z. angew. Chem.*, 1918, 31, i. 50. [2] *Ibid.*, 1918, 31, i. 54.

[3] Scharrnbeck, *Z. ges. Schiess- u. Sprengstoffw.*, 1934, 29, 98, 133. See also Reilly and Rae, *Physico-Chemical Methods*, 1940.

are given by Scharrnbeck.[1] With the exception of the moisture estimation the percentages are calculated on the dry material :—

	Per cent.
Moisture	7·0
Ash	0·6
Wood gum (sulphite cellulose)	5·0
,, ,, (soda cellulose)	6·0
Chlorine—faint opalescence with $AgNO_3$	...
Alkali—faint red colour with phenolphthalein	...
Soluble in alcohol	0·5
Lignin—faint red with phloroglucin reagent	...

Examples of the results obtained with various wood celluloses are also given by Schwalbe and Schrimpff,[2] by Naiman and Troitsky,[3] and by Gabillion.[4]

VIII. Polyhydric Alcohols

(a) Glycerine [5]

Glycerol, $C_3H_5(OH)_3$; mol. wt., 92·09 ; sp. gr., 1·262 ; B.P., 290° ; miscible with water and alcohol ; insoluble in ether.

Pure glycerine is a colourless viscous liquid. The commercial product as used for dynamite is yellow to brownish in colour, and has usually a faint caramel-like odour when rubbed between the hands.

According to Crosfield [6] glycerine for explosives manufacture must be a distilled product as free as possible from water and containing at least 98 per cent. glycerol. Its specific gravity should be not less than 1·262 (15·5°/15·5°). It should be free from lead, calcium, fatty acids, sugars and decomposition products of glycerol (acrolein, etc.) and should not contain more than traces of arsenic, iron and chlorides.

The glycerol content may be determined, if required, by acetylation,[7] or by oxidation with dichromate.[8]

[1] *Loc. cit.*, pp. 34, 267.

[2] *Z. angew. Chem.*, 1918, **31**, i. 50 ; *Z. ges. Schiess- u. Sprengstoffw.*, 1919, **14**, 41 ; 1920, **15**, 17, 38, 53, 91).

[3] *J. Soc. Chem. Ind.*, 1935, 255 T.

[4] *Rev. Chim. Ind.*, 1935, **44**, 310, 330.

[5] Naoum, *Nitroglycerine and Nitroglycerine Explosives*. For the determination of glycerine and glycol *cf.* W. E. Shaefar, *Ind. Eng. Chem.* (*Anal.*), 1937, **9**, 449.

[6] *Z. ges. Schiess- u. Sprengstoffw.*, 1906, **1**, 21 ; see also Lewkowitsch, *Chem. Zeit.*, 1895, **19**, 1423.

[7] Benedikt and Cantor, *Z. angew. Chem.*, 1888, **2**, 460 ; *Monatsh.*, 1888, **9**, 521 ; see also Lewkowitsch, *Chem. Zeit.*, 1889, **13**, 93, 191, 659.

[8] Hehner, *J. Soc. Chem. Ind.*, 1889, **8**, 4.

The water content may be approximately estimated by heating in a weighing bottle with a loose stopper at 90°. Some evaporation of glycerol takes place ; the heating should be continued until the successive losses are very small and approximately constant. The total loss is corrected for the loss of glycerol. Distillation with trichloroethylene has also been proposed.

Reducing substances may be detected by addition of silver nitrate and allowing to stand in the dark for fifteen minutes ; Fehling's solution should give no reduction on standing for twelve hours in the dark.

The organic and inorganic residues are determinated by gradually evaporating 25 g. and completing the evaporation in an air bath at 160°. A little water should be added to the residue from time to time to prevent it from becoming too thick. The residue is weighed, and then ignited to ascertain the percentage of ash. The former should not exceed 0·25 and the latter 0·05 to 0·10 per cent.

Acidity and alkalinity are tested for in the usual way, after diluting the glycerine with two volumes of water. The glycerine should be practically neutral.

Fatty acids are estimated by diluting with an equal volume of water, extracting with ether, washing the ethereal solution several times with water, evaporating off the ether, and drying at 70°. No more than traces should be present.

For the determination of saponifiable matter, 100 g. of the sample is weighed out in a flask, 200 ml. of boiled distilled water and 30 ml. of $N/1$ sodium hydroxide are added ; the whole is maintained at 100° for an hour and titrated.

Sugar and gums are shown by darkening on shaking with concentrated sulphuric acid. Small quantities of polyglycerines may be present, but these do not greatly affect the explosive properties of the nitroglycerine. They raise the specific gravity somewhat, and may therefore cause a glycerine containing a little water to have the correct specific gravity. Glycerine obtained by fermentation contains traces of trimethylene glycol. This gives a dinitrate which is stated to be as stable as nitroglycerine. Albuminous matter is tested for by lead acetate.

The nitrogen content is estimated by the Kjeldahl method, and should not exceed 0·3 per cent. Other tests include sulphides, sulphates, sulphites, thiosulphates, chlorides and arsenic. An important test is the *behaviour on nitration*.[1] A mixture of 1 part by weight nitric acid (sp. gr. 1·50) and 2 parts sulphuric acid (sp. gr. 1·84) is placed in a beaker, which is held in the hand in a pail of cold water and kept continuously in motion. Mixed acid from the factory

[1] Lewkowitsch, *Chem. Zeit.*, 1895, **19**, 1423.

may also be used. The temperature is maintained at 12° to 15° and the glycerine is allowed to flow in slowly. 1 part of glycerine to 8 parts of mixed acid are suitable proportions to employ. Overheating is dangerous and the temperature must not be allowed to exceed 30°. When all the glycerine has been added, the mixture is cooled to 15° and brought into a separating funnel. It is important to observe the readiness with which the nitroglycerine separates from the acids. The separation should take place in ten minutes and should be clean and sharp without flockiness. The acid is carefully run off, and the nitroglycerine is washed repeatedly with water at 40° to 50°, then with lukewarm 2 per cent. sodium carbonate solution, and again with cold water, and measured in a burette. The yield is calculated from the specific gravity of nitroglycerine (1·60). A pailful of water should be held in readiness, in case it is necessary to drown the charge, by reason of the reaction becoming too vigorous. More accurate estimations are obtained by the use of special apparatus in which the nitration is carried out in a separating funnel cooled externally by water or by a freezing mixture. The stirring is effected by compressed air.[1]

The theoretical yield is 246·7 per cent. of the weight of the glycerine. Naoum gives yields of 225 to 229 per cent.

Glycerol may be detected qualitatively in small quantities by colour reactions dependent on the formation of dihydroxyacetone.[2]

(b) Diglycerine [3]

$(CH_2OH\ CHOH\ CH_2)_2O$. Mol. wt., 166·2 ; sp. gr., 1·33 ; B.P., 245° to 250° C. (8 mm.) ; miscible with water ; insoluble in ether.

On heating with small quantities of alkali to 250°-260° glycerine undergoes partial condensation to diglycerine which can be nitrated to diglycerine tetranitrate. This is one of the admixtures which are used to lower the freezing point of nitroglycerine. If the condensation has been carried out with glycerine of good quality, special testing may be confined to the specific gravity (approximately 1·286 at 15° for a content of 30 to 40 per cent. diglycerine). The nitration product gives a nitrogen content of 17·6 to 17·7 per cent. The trial nitration is carried out as described under glycerine. The tetranitrate forms emulsions somewhat readily on washing with water, and it is better to use sodium chloride solution. The tetranitrate retains moisture rather firmly and is more difficult to dry than nitroglycerine.

[1] Naoum, *Nitroglycerine and Nitroglycerine Explosives*; Escales, *Z. ges. Schiess- u. Sprengstoffw.*, 1906, **1**, 23; Novak, *ibid.*, p. 191; Stutzer, *ibid.*, 1910, **5**, 165.

[2] Denigès, *Comptes rend.*, 1909, **148**, 570; *Bull. Soc. Chim.*, 1909 (4) **5**, 421.

[3] Naoum, *Nitroglycerine and Nitroglycerine Explosives.*

(c) Monochlorhydrin [1]

CH_2Cl CHOH . CH_2OH. Mol. wt., 110·5; sp. gr., 1·338; B.P., 213°; miscible with water, alcohol and ether.

Monochlorhydrin consists mainly of α-chlorodihydroxypropane, but contains a small proportion of the β-isomer. Usually a mixture of monochlorhydrin and glycerine is obtained, together with some dichlorhydrin. Small proportions of diglycerine may also be present. Assuming that the monochlorhydrin has been prepared from glycerine of satisfactory purity, it is usually sufficient to ascertain the chlorine content and to ensure freedom from water, hydrochloric acid, and dichlorhydrin. Exact analysis of such a mixture is hardly practicable, but a trial nitration should be included, with a nitrogen determination of the product.

For the determination of chlorine, the mixture is first heated to 115° at 30 mm. pressure. This removes any water and dichlorhydrin. About 5 g. is weighed out and boiled for fifteen minutes with 10 ml. of a 15 per cent. solution of sodium hydroxide in alcohol. The alcohol is evaporated off and a little water is added. This is boiled for a few minutes and the liquid is acidified with nitric acid and the chlorine determined. The value is somewhat too high owing to the presence of small quantities of dichlorhydrin.

(d) Ethylene Glycol [2]

CH_2OH CH_2OH. Mol. wt., 62·0; sp. gr., 1·116 (15°); M.P., −11·5°; B.P., 194°; miscible with water and alcohol.

Ethylene glycol yields on nitration a dinitrate which is used in conjunction with nitroglycerine to lower the freezing point. It is a colourless liquid which is less viscous than glycerine. It resembles glycerine in its hygroscopicity.

It should contain 97 per cent. of ethylene glycol corresponding to a sp. gr. of 1·1074 (20°/4°) if water is the only impurity. The estimation of glycol can be carried out by the dichromate method as for glycerine. It should be free from mineral matter. The moisture content cannot readily be determined by direct heating on account of the greater volatility of ethylene glycol as compared with glycerine. Somewhat more accurate results may be obtained by distilling off a portion of the glycol until pure glycol passes over, then interrupting the distillation and determining the moisture approximately in the distillate by drying in a flat dish over phosphorus pentoxide with daily weighings until the rate of loss is constant. A correction must be applied for the ultimate constant loss.

[1] Naoum, *Nitroglycerine and Nitroglycerine Explosives.* [2] *Ibid.*

A trial nitration is carried out as for nitroglycerine. The yield of nitrate may be depressed slightly by the presence of small quantities of higher homologues.

(e) Pentaerythritol

$C(CH_2OH)_4$. Mol. wt., 136·1; M.P., 253°; soluble in 100 parts water, 5·5 at 15°.

Pentaerythritol is used for the manufacture of the tetranitrate (Penthrit) which is a powerful explosive. It is a white or slightly yellowish crystalline compound. The melting point should be at least 220° to 230° and the compound should be completely soluble in water. According to Pushin,[1] pentaerythritol undergoes allomorphic transformation at 185° and melts at 256°.

IX. Aromatic Hydrocarbons and Derivatives

(a) Hydrocarbons

Benzene and toluene are used for the manufacture of nitro-compounds; xylene is used to a minor extent. They are colourless liquids and should be completely neutral. They are insoluble in water, but mix with most organic solvents.

	Benzene	Toluene	Xylene
Melting point	5·2°	−94°	...
Boiling point	80·4°	110·3°	136° to 140°
Sp. gr. (20° C.)	0·879	0·866	0·868

In the distillation of benzene and toluene 90 per cent. should pass over within a range of 0·6°. For the distillation, 100 ml. are placed in a distillation flask of about 200 ml. capacity. This rests on a sheet of asbestos with a hole of 1 in. diameter in the centre. The flask is surrounded by an aluminium cylinder which reaches nearly to the level of the side tube. Xylene is a mixture of isomers of somewhat indeterminate boiling point.

Small percentages of *aliphatic hydrocarbons* are usually present. These should be as low as possible, as they do not undergo nitration. The specific gravity gives some indication of their presence, but a trial nitration is more certain. The hydrocarbon is nitrated to the mono-nitro-compound by a mixture of concentrated sulphuric acid and nitric acid (sp. gr. 1·42) at about 10° with vigorous stirring. The mixed acid is added very slowly to the hydrocarbon and the stirring is continued for an hour after all the acid has been added. The acid is drawn off, and the nitro-compound washed with water with addition of soda to render it alkaline. The separated oil is steam distilled until the drops sink in water. The water is separated and the oil is treated

[1] *Bull. Soc. Chim. Yougoslav.*, 1934, 5, 83.

again with nitration acid in a graduated cylinder. The unnitratable hydrocarbons form the top layer.

An alternative method is by sulphonation. Evans[1] describes the following method for toluene. A measured quantity (about 50 ml.) of toluene is added to 150 ml. of 98 per cent. sulphuric acid in a 250 ml. graduated cylinder. The cylinder is carefully shaken, so that the temperature does not exceed 45° and the stopper is lifted frequently to avoid excess pressure. The cylinder is allowed to stand for five minutes and vigorously shaken for three to four minutes. The liquid is transferred to a separating funnel, the neck of which is narrow and graduated in 1/100 ml. The bottom outlet of the funnel is connected by a rubber tube with a mercury reservoir. By this means the acid can be raised until the paraffin layer is contained in the narrow neck. The volume is read after two to three hours. A correction for solubility of 0·6 of the percentage of paraffins found is allowed.

Thiophene is detected by shaking in the cold with a sulphuric acid solution of isatin. This gives a blue coloration in presence of thiophene. This may be used as a colorimetric method for the estimation of thiophene.[2]

Naphthalene is also used for the manufacture of nitro-derivatives. It should be in the form of pure white crystals of melting point 79° or over. It should not become yellow on exposure to air and light. It should give no residue on sublimation. A solution in concentrated sulphuric acid should give only a faint red colour. On boiling with water it should give no acidity. It should dissolve completely in benzene to a colourless clear solution. Naphthalene forms a sparingly soluble picric acid compound, which can be made use of in its estimation.

(b) Phenol

C_6H_5OH. Mol. wt., 94·02 ; sp. gr., 1·066 (15°) ; M.P., 41° ; B.P., 181·5° ; soluble in 100 parts water at 15°, 10·3 ; completely miscible at 84°.

Pure phenol forms colourless crystals ; the commercial product has as a rule a slight reddish colour. A setting point of 40° is usually specified ; a lower setting point indicates the presence either of water or of cresols. It should give a clear solution in 10 per cent. sodium hydroxide solution.

Phenol is used for the manufacture of picric acid. Metacresol can be similarly converted to trinitrometacresol. Technical metacresol contains ortho- and paracresol. On nitration these isomers are oxidized to oxalic acid. An approximate estimate of the content of metacresol can be obtained by a trial nitration[3] under definite

[1] *J. Soc. Chem. Ind.*, 1919, **38** T., 402.
[2] Dimroth, *Ber.*, 1902, **35**, 2035.
[3] *Z. angew. Chem.*, 1900, **13**, 759.

conditions. The pure metacresol gives 174 per cent. by weight of trinitro-compound, and the yield is proportional to the meta-content in mixtures of the isomers.

(c) Dimethylaniline

$C_6H_5N(CH_3)_2$. Mol. wt., 121·0; sp. gr., 0·955; M.P., 2°; B.P., 193°; slightly soluble in water; soluble in organic solvents.

Dimethylaniline serves for the preparation of tetryl (trinitrophenyl methylnitramine). It may contain water, aniline and monomethylaniline. It should be light in colour, free from mineral matter, and should give a clear solution when mixed with an equal volume of concentrated hydrochloric acid.

The presence of aniline is shown by the carbylamine reaction. Aniline and monomethylaniline react with acetic anhydride. An approximate estimate can be obtained by the rise of temperature when 50 ml. of the dimethylaniline and 10 ml. of acetic anhydride are brought together in a Dewar vessel. A comparative experiment should be made with dimethylaniline containing a known amount of monomethylaniline. Alternatively the amount of acetic anhydride used up may be determined by filtration. A weighed quantity of acetic anhydride (about 2·5 g.) is added to a weighed quantity of dimethylaniline (about 10 g.). The acetylation is allowed to proceed for two to three hours, 70 ml. of water added and the whole warmed on a water-bath for half an hour and then titrated with sodium hydroxide. This gives the quantity of acetic anhydride not used in acetylation.

X. Solvents

(a) Acetone [1]

CH_3COCH_3. Mol. wt., 58·08; sp. gr., 0·7912 (20°/4°)[1]; B.P., 56·1°; soluble in water and organic solvents. For acetone and water density tables see Reilly and Ralph.[2]

Acetone should be colourless and completely miscible with water. Its specific gravity should not exceed 0·800 at 15°. It should give no turbidity on mixing with twenty times its volume of carbon disulphide, and no residue on evaporation. It should be free from acidity, except for traces of dissolved carbon dioxide (approximately 0·01 per cent.). To test acidity the acetone is boiled to remove carbon dioxide, diluted with an equal volume of water (free from carbon dioxide) and titrated with alkali, using phenolphthalein as indicator. Alkalinity should be absent, as it indicates the presence of amines; it is tested for by diluting and adding methyl red or para-nitrophenol.

Alcoholic impurities are detected by means of a reagent made

[1] Cf. *British Standards Institution*, Specification for Acetone, *B.S.* 509, 1933.

[2] *Sci. Proc. Roy. Dub. Soc.*, 1919, **15**, 597.

up by dissolving 0·5 g. of potassium dichromate in 100 ml. of nitric acid (sp. gr. 1·332). 1 ml. of the acetone is mixed with 3 ml. of the reagent, and allowed to stand for five minutes. No blue or violet colour should be formed.

Aldehydes and similar reducing substances are tested for by the permanganate test. A solution of 1 g. potassium permanganate in a litre of water is made up and 1 ml. of this is added to 100 ml. of acetone. The colour should persist for at least thirty minutes at 15·5° in the dark. In Germany, a silver nitrate test is included to detect aldehydes: these can also be detected by Schiff's reagent (fuchsine-bisulphite). "Light oils" also reduce ammoniacal silver nitrate. They may be tested for as follows.[1]

Method 1. 100 ml. acetone and 200 ml. water are mixed and rapidly distilled in a retort. The first 10 ml. of distillate is collected in a graduated cylinder, 20 ml. of water added, and the volume of any oil which separates on standing is measured.

Method 2. 10 ml. of acetone is added to 100 ml. of water at 15°. 2 ml. of a solution containing 12·69 g. iodine and 14·60 g. potassium iodide is added. After exactly one minute, 2 ml. of $N/10$ thiosulphate is added and the excess of thiosulphate titrated with iodine. 1 ml. of $N/100$ iodine solution is equivalent to approximately 0·02 per cent. of the impurity.

The acetone content is usually estimated by Messinger's method.[2] 2 g. of acetone is mixed with 500 ml. water; 10 ml. of the mixture is mixed with 25 ml. $N/1$ alkali and 50 ml. $N/10$ iodine added with shaking. The mixture is shaken frequently and after fifteen to twenty minutes 26 ml. of $N/1$ sulphuric acid added. The iodine is titrated with thiosulphate. The acetone is converted to iodoform; six atoms of iodine correspond to one mol. of acetone.

A method depending upon the action of mercuric sulphate[3] is also stated to give satisfactory results.

Acetone may be detected qualitatively either by the above reactions or by the following test: The liquid is diluted with water, 2 drops of 5 per cent. nitroprusside, 2 drops of 5 per cent. sodium hydroxide and 5 or 6 drops of acetic acid are added. Acetone gives a red colour changing to violet on warming.

(b) Ethyl Ether[4]

$(C_2H_5)_2O$. Mol. wt., 74·12; sp. gr., 0·713/15°; B.P., 34°; partially soluble in water; miscible with most organic solvents.

The liquid should be clear and colourless. The specific gravity is usually prescribed (*e.g.* 0·722) at 15°. The boiling point should be

[1] Marshall, *Explosives*.
[2] *Ber.*, 1888, **21**, 3366.
[3] Votocek and Kasparak, *Bull. Soc. Chim.*, 1923, (4) **33**, 110; Jonesco, Matiu, *Z. anal. Chem.*, 1927, **72**, 439.
[4] Cf. *British Standards Institution*, Specification for Technical Ether, *B.S.* 579, 1934.

between 34° and 36°. The residue on evaporation should not exceed 0·002 per cent. On shaking with water, the aqueous extract should not be acid to litmus. In some specifications the acid is limited to 0·006 per cent. (as CH_3COOH).

Water may be tested for by anhydrous copper sulphate or by aluminium ethylate.[1] Alcohol may be detected by the iodoform reaction, but acetaldehyde also gives this reaction. Acetaldehyde gives a greyish precipitate of mercury with Nessler's reagent. Schiff's reaction may also be used. In Germany, a test which is used for acetaldehyde and vinyl alcohol is to add 5 g. solid potassium hydroxide to 30 ml. of ether and allow to stand in the dark with shaking. After an hour there should be no separation of yellow or brown solid.

Hydrogen peroxide and organic peroxides may be detected by potassium iodide. Middleton [2] gives the following method: 130 ml. of 2·5 per cent. sulphuric acid is boiled, carbon dioxide being bubbled through the liquid. 5 g. of ferrous sulphate is dissolved in it, and after cooling to 40°, 30 ml. of a 10 per cent. solution of potassium thiocyanate added, and then, drop by drop, a *N*/300 solution of titanous chloride until the brown colour disappears. 5 ml. of this reagent is put into a 35 ml. flask which is then filled with ether to the neck and allowed to stand for five minutes with occasional shaking. Peroxides are indicated by a brown colour, and may be determined by titration with *N*/300 titanous chloride.

Sulphur compounds are tested for by shaking with mercury. One drop of mercury should give no discoloration when shaken in presence of air with 10 ml. of ether which has been acidified with a few drops of acetic acid.

(c) Ethyl Alcohol

C_2H_5OH. Mol. wt., 46·07; sp. gr., 0·789 at 20°; B.P., 78·3°; miscible with water and with most organic solvents with which it forms azeotropic mixtures.[3]

The liquid should be clear and should give no turbidity with water. It should give no smell of fusel oil, and practically no residue on evaporation (0·01 per cent.). It should be as free as possible from acidity.

Fusel oil may be detected by adding water, shaking out with chloroform, separating, and allowing the chloroform to evaporate. The residue with addition of dilute sulphuric acid should give no smell of fusel oil. Fusel oil may be estimated quantitatively by oxidation to valeric acid.[4]

Acetaldehyde and other aldehydes are tested for by ammoniacal silver nitrate; this should not become coloured or turbid on standing for a short time. Nessler's reagent should give only a slight precipitate.

[1] Henle, *Ber.*, 1920, **53**, 719.
[2] *Pharm. J.*, 1924, **113**, 98.
[3] Reilly, *Distillation*, London, 1936; *cf.* Reilly, Kelly and Ryan, *J. Soc. Chem. Ind.*, 1937, **56**, 231 T.
[4] Marquardt, *Ber.*, 1882, **15**, 1370, 1661.

Schiff's reagent may also be used. Siebert[1] recommends a method in which the aldehyde is converted to aldoxime by hydroxylamine hydrochloride. Acid is liberated in the reaction, and is titrated with sodium hydroxide.

Acetone gives a red colour with sodium nitroprusside and alkali : aldehyde reacts similarly. More distinctive is the vanillin reaction[2]; 2 ml. of a solution of 15 g. vanillin in 100 ml. alcohol is mixed with 3 ml. of the liquid under test and 1 ml. conc. sulphuric acid. Acetone gives a carmine red colour, which turns yellow on addition of water. Alkali turns the colour bright orange red.

Methyl alcohol may be detected and estimated by conversion to methylaniline by means of iodine, phosphorus and aniline, followed by oxidation by stannic chloride to methyl violet.[3] Other methods depend upon the conversion of the methyl alcohol to formaldehyde, which gives various colour reactions, *e.g.* with morphine sulphate[4] and with fuchsine bisulphite.[5]

Benzene may be separated by shaking with a concentrated solution of calcium chloride. For small quantities the alcohol is diluted with water, a small proportion is distilled over and the distillate shaken with potassium dichromate and hydrochloric acid. After fifteen minutes the solution is shaken with petroleum ether and the increase in volume of the petroleum ether layer is measured.[6]

Ethyl alcohol may be identified in mixtures by conversion to ethyl benzoate or ethyl-*p*-nitrobenzoate by the Schotten-Baumann reaction.

B. ANALYSIS OF EXPLOSIVES

I. BLACK POWDER

Black powder consists of a mixture of nitre, charcoal and sulphur. The proportions vary somewhat, the nitre being generally about 74 to 78 per cent., the charcoal 12 to 16 per cent., and the sulphur 9 to 12 per cent. Allied mixtures are met with containing sodium nitrate in place of potassium nitrate, coal or soot in place of charcoal and occasionally other ingredients, such as resin, pitch, cellulose, etc. The influence on gun-powder of various constituents and their amounts has been discussed by Hoffman.[7]

[1] *Chem. Zeit.*, 1921, **45**, 349.
[2] Kutscheroff, *Z. anal. Chem.*, 1905, **44**, 622 ; Kolthoff, *Pharm. Weekblad*, 1918, **55**, 1021.
[3] Riche and Bardy, *Comptes rend.*, 1875, **80**, 1076.
[4] Kentmann, *Pharm. Generalanz.*, 1896, **8**, 356 ; Rabe, *Pharm. Zeit.*, 1921, **66**, 72, 135.
[5] Denigès, *Bull. Soc. Chim.*, 1910, (4) **7**, 951 ; *Comptes rend.*, 1910, **150**, 832.
[6] Babington and Tingle, *Ind. Eng. Chem.*, 1919, **11**, 555.
[7] *Sitzungsber. Preuss. Akad. Wiss.*, 1930, **25**, 432.

(a) General Examination

The powder should show no differences in colour even when pulverized between the fingers. The grains should be hard, and on grinding the powder should break first into sharp-edged fragments. When poured over a sheet of white paper it should not leave traces of black dust. The size of grain is measured by sieving. The apparent density is found by pouring the powder into a measuring vessel, striking off the excess with a straight-edge, and weighing.

The "absolute" density is measured by displacement of mercury. An apparatus for this purpose was devised by Bianchi.[1] In this method the air is removed from the interstices by evacuation. In the method used by the U.S.A. Bureau of Mines [2] a vacuum pump is not required. These methods give figures of 1·65 to 1·85. This is not, however, the true absolute value, as the mercury does not penetrate into the finer interstices.[3]

Gun-powder tends to absorb moisture in a damp atmosphere. The hygroscopicity may be determined by placing a weighed quantity on a small tray with a bottom of fine wire gauze enclosed in a box containing a saturated solution of potassium nitrate. The powder is left in the box for one to two days, according to the size of the grains, and is then weighed. Alternatively the gun-powder may be placed in a saturated atmosphere in comparison with a standard sample.

After storage in a damp atmosphere efflorescence of potassium nitrate crystals may occur. This can be detected under the microscope. Except for such efflorescence there is no tendency for the ingredients to segregate. If stored in contact with metals some reduction of the nitrate to nitrite may occur.

(b) Chemical Examination [4]

Moisture. As sulphur is slightly volatile at 100° the moisture is estimated by heating at 70° for one and a half to three hours, or by drying in a desiccator over sulphuric acid for three days. Limits range from about 0·8 to 1·2 per cent.

Acidity. When the powder is extracted with water, the solution should not be more than very faintly acid to litmus paper.

Potassium Nitrate. 10 g. of the powder is extracted with warm water in a Gooch crucible, about 200 ml. of water being added in quantities of 15 to 20 ml. at a time. The final washings should give

[1] *Cf.* Marshall, *Explosives*, Second Edition, p. 412.
[2] *Int. Cong. Appl. Chem.*, VIII., 1912, 4, 105.
[3] *Cf.* also Reilly and Rae, *Physico-Chemical Methods*, 1938.
[4] *Cf.* also *U.S. Bur. Mines, Bull.* 51, 69; *Bull.* 219, 143.

no residue on evaporation. The diphenylamine test may also be used to see if the extraction is complete. The loss of weight of the crucible and contents, after drying at 70°, gives the percentage of potassium nitrate after allowing for the moisture content. As the charcoal contains a little water-soluble matter, it is necessary, for accurate determinations, to evaporate an aliquot portion of the filtrate and to heat it to incipient fusion. An estimate of the nitrate by means of the nitrometer is occasionally included.

The nitrate may be tested for chloride, sulphate, perchlorate, etc. (see Potassium Nitrate, p. 489).

The dried material in the crucible is extracted with carbon disulphide which has been recently distilled, until the washings give no residue of sulphur. The residue is dried in a warm place (avoiding flames) and finally at 100°. The loss of weight gives the sulphur.

In Gay-Lussac's method, 5 g. of the fine powder is mixed with 5 g. dry sodium carbonate. 5 g. pure potassium nitrate and 30 g. sodium chlorate are added and the whole well mixed in a mortar, and ignited in a platinum crucible. After cooling, the mixture is dissolved in water, oxidised with bromine solution, acidified, and the sulphate estimated as barium sulphate.

Another method is to oxidise the original powder with 11 parts of pure conc. nitric acid and 2 parts of potassium chlorate until the liquid is clear and yellowish. The nitric acid is evaporated and the sulphur determined as sulphate. Petersen [1] boils the powder with sodium hydroxide and hydrogen peroxide, and estimates as sulphate. Oehman [2] gives a method in which the water-insoluble material is burnt in a bomb calorimeter.

Charcoal. This forms the residue after extraction of the potassium nitrate and sulphur. It should be examined for ash and total carbon content. It is also examined microscopically for wood meal, soot, etc.

It is sometimes preferred to proceed as follows: after the moisture estimation, a separate sample of 2·5 g. of the powder is extracted with carbon disulphide and the insoluble part weighed. From this the sulphur is calculated. For the nitrate, 2·5 g. is shaken with 250 ml. of water and left overnight. An aliquot part is then evaporated to dryness and weighed. If desired, the nitrate may be converted to sulphate by adding sulphuric acid, drying and igniting; this removes organic matter. The charcoal is determined by difference.

[1] *Z. anal. Chem.*, 1903, **42**, 406.
[2] *Chem. Zeit.*, 1931, **55**, 394.

II. Nitric Esters

(a) Nitrocellulose

Nitrocellulose, as prepared from cellulose by nitric and sulphuric acids, consists of small fibres similar to the original cellulose. A microscopic examination gives an indication of the nature of the cellulose used for nitration. The length of fibre shows whether the pulping has been efficient. Apart from its rapidity of burning nitrocellulose may be distinguished from cellulose by acetone or ethyl acetate. These solvents gelatinise nitrocellulose, but do not affect cellulose. It may also be tested for nitrogen by diphenylamine and sulphuric acid. Some information as to the degree of nitration may be obtained by examination under polarised light.[1]

Ungelatinised nitrocellulose will usually be received in the wet condition. The moisture can be determined, if required, by mixing the sample thoroughly, rubbing through a metal sieve, weighing out about 10 g. rapidly, and drying in a steam oven. Sometimes a lower temperature (50°) or evacuation over sulphuric acid is prescribed. If the stability of the dried nitrocellulose is to be determined, calcium chloride should be used as drying agent.

For the chemical tests, the sample is prepared by squeezing out the moisture as far as possible between layers of pure filter paper, teasing out loosely, drying at 50° and transferring to a desiccator. A review of the methods of testing is given by Schrimpff.[2]

Mineral Matter. About 3 g. of the nitrocellulose is weighed into a tared silica dish, covered with a layer of molten paraffin wax, stirred and ignited, care being taken to avoid loss. After all has burnt off, the contents of the dish are moistened with ammonium carbonate, dried and treated to 105-110°. Sometimes sulphuric acid is used for moistening, and the residue ignited. Another method is to moisten the nitrocellulose with nitric acid and heat on the water-bath. The residue is then ignited. After cooling, a little water is added, evaporated, and the residue again ignited.

Calcium Carbonate. 10 g. of nitrocellulose, 100 ml. of $N/10$ hydrochloric acid and 100 ml. water are put into a stoppered cylinder, shaken for an hour, and the excess of acid titrated with $N/10$ sodium carbonate, using methyl orange as indicator.

Soluble Salts. Nitrates are sometimes mixed with nitrocellulose and may be determined by extraction with water.

[1] Lunge and Weintraub, *Z. angew. Chem.*, 1899, **12**, 467; de Chardonnet, *Comptes rend.*, 1907, **145**, 115; Ambronn, *Kolloid Z.*, 1913, **13**, 210; Tissot, *Mém. Poudres*, 1927, **22**, 31: Desmaroux, *Mém. Poudres*, 1928, **23**, 4.

[2] *Z. ges. Schiess- u. Sprengstoffw.*, 1920, **15**, 17, 38, 53, 91.

Paraffin Wax. A coating of wax is sometimes present ; this can be extracted with ether.

Stability Tests. The tests are described in Section C (p. 558 *et seq*.). The Heat test, Bergmann and Junk test, and Will test are frequently applied. A limit of 10 mins. at 170° F. is laid down by the Home Office for the Heat test.

Nitrogen. Numerous methods have been applied to this determination. These are fully described by Reinhold.[1] They include gravimetric methods (nitron), volumetric methods depending on reduction of the nitric acid to ammonia, and gas volumetric methods. The methods most commonly used are the nitrometer method (Lunge) and modifications of the Schulze-Tiemann method, depending on the action of ferrous chloride.

Nitrometer method. The apparatus is described in Vol. I., p. 78.[2] The nitrocellulose is passed through a sieve and dried. About 0·6 g. is weighed into a small weighing bottle. To ensure complete drying the bottle and contents may be dried for an hour in a steam oven and weighed. Concentrated sulphuric acid (6 to 8 ml.) is added and allowed to stand for twenty to thirty minutes to dissolve the nitrocellulose. The solution is washed with small quantities of sulphuric acid into the cup of the nitrometer and allowed to flow into the bulb. This should be done without delay. About 0·5 ml. water is added to the last portion of sulphuric acid. The nitrometer is shaken and the nitric oxide is measured in the usual way. The shaking should not be too prolonged, as this decreases the gas volume. The nitric oxide contains traces of other gases (carbon monoxide, etc.) which tend to increase the gas volume ; on the other hand, a little nitric oxide is absorbed by the sulphuric acid. The solubility is at a minimum in 85 per cent. sulphuric acid. Webb and Taylor [3] recommend the use of 91 to 92 per cent. sulphuric acid, and allow 0·2 ml. in 10 ml. acid for the solubility. The accuracy of the nitrometer method has been studied by Beckett [4] and Rubens.[5]

In the Du Pont nitrometer [6] direct readings of the nitrogen percentage can be made without the necessity of correcting the volume of gas to standard temperature and pressure.[7] The apparatus consists of (1) a generating bulb with mercury reservoir attached, as in Lunge's nitrometer, and (2) a reading apparatus, with a closed compensator

[1] *Nitrocellulose*, 1931, **2**, 149, 171, 214, 232 ; *cf.* also Marqueyrol, *Mém. Poudres*, 1924, **21**, 326. [2] *Cf.* also Lunge and Ambler, *Technical Gas Analysis*, p. 370.

[3] *J. Soc. Chem. Ind.*, 1922, **41**, 362.

[4] *J. Soc. Chem. Ind.*, 1914, **33**, 628 ; *J. Chem. Soc.*, 1920, **117**, 220.

[5] *Z. ges. Schiess- u. Sprengstoffw.*, 1933, **28**, 172.

[6] Pitman, *J. Soc. Chem. Ind.*, 1900, **19**, 982 ; *cf.* Scott, *Standard Methods of Chem. Analysis*, 4th Edition, p. 354.

[7] *Cf.* Lunge's Gas Volumeter, described in Vol. I., p. 83.

bulb containing dry air. The generating bulb has a two-way stopcock, connecting either with the cup or with an exit tube. The sample is introduced and shaken with mercury and sulphuric acid. The quantity must be such that the gas volume is between 171·8 and 240·4 ml. The nitric oxide is transferred to a reading burette, which is connected at its lower end by rubber tubing to (1) a mercury reservoir and (2) a closed compensator bulb with a lower tube which is marked with a graduation mark. The levels are adjusted so that the mercury is at the level of the graduation mark on the compensator tube, and is at the same time balanced between this and the reading burette. The reading is then taken. The reading burette is calibrated from 10 to 14 per cent. of nitrogen for 1 g. of substance. The instrument is standardized by carrying out a measurement with pure potassium nitrate.

The Schulze-Tiemann method [1] depends upon the action of boiling ferrous chloride solution in presence of hydrochloric acid. This converts the nitrogen of the nitrocellulose to nitric oxide. The method has been modified from time to time; the modification introduced by Schmidt [2] has been much used, and further improvements have been introduced by Jacqué,[3] Schrimpff,[4] Reinhold,[5] Lenze and Rubens.[6]

The apparatus used in Reinhold's method is shown in Fig. 119. The vessel in which the gas is evolved consists of a round-bottomed flask of 300 ml. capacity made of Jena glass with a long neck. The stopper is of glass and is connected with two glass tubes as shown. The connection between stopper and flask is made by means of a short length of rubber tube which is fitted between the two and makes a gas-tight joint.

The tube A is connected by a rubber tube with a glass tube about 12 cm. long, constricted at the end, and dipping into a small beaker of water. The tube B is connected by a rubber tube with a forked glass tube. One of the branches is connected to a drawn-out tube dipping into water. The other is joined by a short rubber tube to the measuring apparatus. Spring clips are affixed to the rubber joints as shown.

The flask is clamped over a bunsen burner with a small flame. The measuring apparatus consists of the measuring tube (M), the levelling tube (N), and a connecting tube (Z) of special construction,

[1] Schlösing, *Ann. Chim. Phys.*, 1853, (3) **40**, 479; Schulze, *Z. anal. Chem.*, 1870, **9**, 401; Tiemann, *Ber.*, 1873, **6**, 1041; Scheiding, *Z. angew. Chem.*, 1890, **3**, 614; Glaser, *Z. anal. Chem.*, 1892, **31**, 285.

[2] Guttmann, *Manufacture of Explosives.*

[3] *Int. Congr. Appl. Chem.* VI., 1907, vol. i., section i., p. 264.

[4] *Z. ges. Schiess- u. Sprengstoffw.*, 1920, **15**, 19.

[5] *Nitrocellulose*, 1931, **2**, 232.

[6] *Z. ges. Schiess- u. Sprengstoffw.*, 1932, **27**, 114; 1933, **28**, 172.

which enables the flask in which the gas is evolved to be connected with the measuring tube. The upper portion of the measuring tube is widened, and the calibrations commence at 100 ml. at the place where

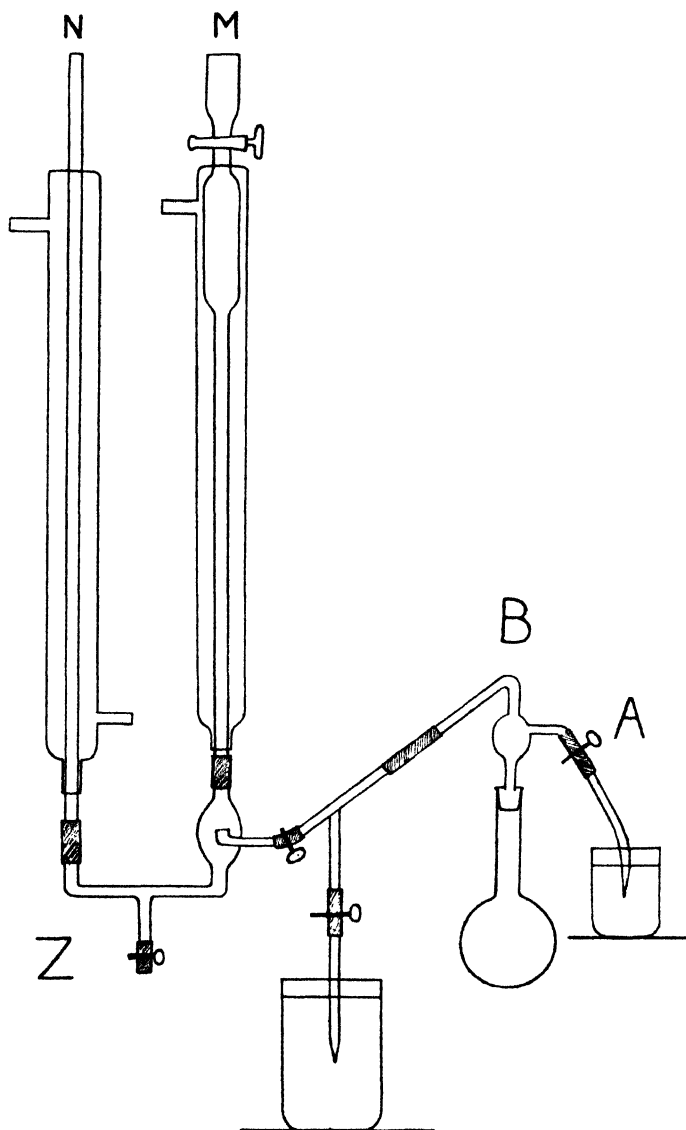



FIG. 119.

the tube narrows, and extend to 130 or 150 ml. The tube is jacketed as shown, to permit of cooling by water. The levelling tube is of the same internal diameter as the measuring tube, and is also jacketed. The tube with pinch-cock at the bottom serves to draw off the liquid

as required. The liquid consists of 30 per cent. potassium hydroxide. The measuring tube and levelling tube are filled and the tube leading to the flask is filled as far as the junction of the two tubes.

The nitrocellulose is dried and 0·6 g. weighed into the flask, 30 ml. of water being then added. The apparatus is connected up as shown. The flask is heated over a free flame, the clips remaining open. When all the air has been expelled, both clips are closed and the flame is simultaneously removed ; 25 ml. of concentrated ferrous chloride is put into the smaller beaker and sucked into the flask by opening the clip cautiously to avoid influx of air. Thereupon 20 ml. conc. hydrochloric acid is introduced in the same way, and finally a small quantity of water. The flask is then heated carefully until the rubber connections show signs of a positive pressure, and on cautious opening of the pinch-cock no more liquid enters the flask. The pinch-cock connecting the flask with the measuring tube is opened, and the nitric oxide is driven over, the contents of the flask being vigorously boiled. At the same time the cooling water is set in action, and a thermometer suspended in the cooling-jacket. When no more gas passes over, the pinch-cock is closed, the flame is removed, and the flask allowed to cool somewhat. This sets free the dissolved nitric oxide, and the flask is again heated to drive over the remaining nitric oxide. When the gas evolution comes to an end, the pinch-cock is closed, and the flame is turned out, and the alkaline liquid is drawn off from the cock at the bottom of the measuring tube and levelling tube, until the liquids are at the same level in both tubes. The volume of gas can be read off at once. The temperature and barometric pressure are also read. The two tubes should be at approximately the same temperature. The nitrogen content is readily calculated from the volume of nitric oxide.

The ferrous chloride solution is made by warming conc. hydrochloric acid with excess of iron nails, filtering, and adding a little conc. hydrochloric acid. It should be moderately fresh. All solutions must be free from dissolved air.

The Schulze-Tiemann method is generally found to give somewhat low results, compared with the nitrometer.

For the determination by the nitron method[1] 0·2 of nitrocellulose is brought into a 150 ml. Erlenmeyer flask with 5 ml. of 30 per cent. sodium hydroxide solution and 10 ml. of 3 per cent. hydrogen peroxide, warmed for a few minutes on the water-bath until frothing ceases, and then boiled on a free flame. The nitrocellulose should pass into solution in a few minutes. After cooling, 40 ml. of water and 10 ml. of hydrogen peroxide solution are added, the solution warmed to 50° and 40 ml. of 5 per cent. sulphuric acid allowed to flow into the

[1] Schrimpff, *Z. ges. Schiess- u. Sprengstoffw.*, 1920, **15**, 38.

bottom of the flask by a pipette. The solution is further warmed to 80° and 12 ml. of nitron acetate added (10 per cent. solution of nitron in 5 per cent. acetic acid). After cooling and standing for one and a half to two hours (preferably at 0°) the nitron nitrate is filtered off and washed three or four times with 10 ml. of ice-cold water. The precipitate is dried at 110°. From the weight of the $C_{20}H_{16}N_4HNO_3$ (mol. wt. 375) the nitrogen content of the nitrocellulose is calculated.

Unnitrated Cellulose. 5 g. of nitrocellulose is boiled for half an hour with a saturated solution of sodium sulphide, allowed to stand for twenty-four hours, the solution decanted, and the residue boiled again with fresh sodium sulphide. The insoluble matter is collected on a linen filter of known weight, washed with hot distilled water until free from sulphide, then with dilute hydrochloric acid and finally with water until free from chloride. The residue is dried at 50° and weighed. It is then ignited in a platinum crucible and the weight of the ash deducted from that of the total residue.

According to Lunge and Weintraub [1] the sodium sulphide method is inaccurate, as the residue contains nitrocellulose. They therefore worked out a method in which the nitrocellulose is treated with sodium ethylate and acetone.

Another method [2] is to boil 5 g. nitrocellulose for forty minutes with 30 ml. of a solution of stannous chloride in excess of sodium hydroxide, allow to stand for twenty-four hours, decant carefully, boil the residue again with 30 ml. of the solution, filter, wash with water, then with 5 per cent. hydrochloric acid and again with water, dry and weigh. Then ignite and deduct the weight of the ash.

The unnitrated cellulose may also be determined by dissolving the nitrocellulose in acetone. 5 g. of nitrocellulose is treated with a litre of acetone and allowed to stand for twenty-four hours with frequent shaking. The solution is decanted, the residue filtered, washed with acetone, dried at about 70°, and weighed.

Solubility in Ether-Alcohol. The lower nitrates of cellulose are in general more readily soluble in a mixture of ether and alcohol than the higher nitrates. The general method of testing is to introduce a weighed quantity of nitrocellulose into a measuring cylinder and shake with a mixture of ether and alcohol. The temperature at which this is done is of importance; sometimes 15·5° is specified, and sometimes 20°. After shaking at frequent intervals for six hours, the cylinder is allowed to stand overnight to allow the insoluble nitrocellulose to settle, and an aliquot portion of the clear liquid is withdrawn and evaporated. Usually the bulk of the liquid is distilled off in a flask on a water-bath, and the remainder is washed into a glass dish with ether-alcohol and evaporated to dryness. It is advisable

[1] *Z. angew. Chem.*, 1899, **12**, 473. [2] Böttger, *Z. anal. Chem.*, 1874, **13**, 339.

to add a little water before or during the evaporation, as this causes the nitrocellulose to separate out in a looser condition in which it can be more readily dried. The temperature is finally raised to 80° and the dish is then cooled in a desiccator and weighed.

The quantity of nitrocellulose and the proportions of ether and alcohol vary somewhat, *e.g.* 2 to 4 g. may be treated with 150 ml. of ether-alcohol (2 : 1). In Germany the proportion of ether to alcohol is 4 : 3, 2 g. of nitrocellulose being shaken with 215 ml. alcohol and 285 ml. ether. In some cases it is preferred to shake first with alcohol and then add the required quantity of ether, as this avoids the formation of gelatinous lumps.

The above method is in general use for gun-cotton, which is mainly insoluble in ether-alcohol. It may also be used for nitrocelluloses which are almost completely soluble, but alternative methods have been devised for the latter in which the insoluble portion is estimated.[1] Thus, after treatment with ether-alcohol and settling, the clear liquid may be siphoned off and the residue again treated with ether-alcohol, the treatment being repeated as required. The residual suspension is ultimately filtered through a filtering tube fitted with a plug of asbestos, and the insoluble matter dried and weighed. A shortened method is also described in which the liquid, after standing, is transferred to a tube which is tapered at the bottom to a narrow graduated portion. An approximate estimate of the insoluble nitrocellulose may be obtained from the volume which it occupies in the narrow part of the tube.

Sulphates. These include sulphuric esters together with any inorganic sulphate ($CaSO_4$). Dunnicliff[2] gives the following method : 5 g. of nitrocellulose is heated on a water-bath with 50 ml. conc. nitric acid until the nitrocellulose has dissolved and brown fumes have ceased. About 1 g. sodium chlorate is added in small quantities and the whole evaporated to dryness. The residue is treated with 20 ml. of hydrochloric acid and 0·5 sodium chlorate (added in small quantities) and the liquid again evaporated to dryness. This latter treatment is repeated. This converts all sulphuric esters to soluble sulphate, which may be estimated in the usual way. A blank test is made to allow for sulphate in the reagents.

An alternative method is to destroy the nitrocellulose by boiling with nitric acid containing potassium nitrate, heat the residue strongly, dissolve in hydrochloric acid, filter, and determine the sulphate.[3]

Mercury. Traces of mercury mask the heat test, and it is important to ensure its absence. Probably the most sensitive method for the detection of mercury is to examine the spectrum given by an electrical

[1] Scott, *Standard Methods of Chemical Analysis*, vol. ii.
[2] *Analyst*, 1925, 543. [3] Piest, *Z. angew. Chem.*, 1913, **26**, 661.

discharge through a vacuum tube containing the material under test, the latter being kept at a temperature of 100°. Alternatively the explosive under test may be heated in a vessel in which gold leaf is placed, and the gold leaf subsequently tested in the vacuum tube.[1] In the latter method the presence of mercury is also shown by whitish-grey spots of amalgam on the gold.

Viscosity. The nitrocellulose is dissolved in ether-alcohol or acetone and the viscosity determined in a viscometer. It is usual to find the time required by a steel ball to drop through a measured height of the solution.[2] Viscosities of nitrocellulose solutions are given by Baker.[3]

For the detection of nitrocellulose in explosives, Stansky[4] recommends extracting with acetone, evaporating the solution to a small bulk and adding chloroform to precipitate the nitrocellulose. This is then hydrolysed with sodium hydroxide solution, and tested for nitrate by diphenylamine and sulphuric acid.

(b) Nitroglycerine

Glyceryl trinitrate, $C_3H_5(NO_3)_3$. Mol. wt., 227·0; sp. gr., 1·600; M.P., 13°; soluble in 100 parts water, 0·14 at 15°, 0·35 at 90°; soluble in organic solvents.

Nitroglycerine seldom comes into commerce as such. The examination of nitroglycerine is therefore as a rule necessary only in works laboratories. If it is in solution in alcohol or acetone, it should be separated by dilution with water and filtered through dry salt.

Nitroglycerine should form a clear, or very slightly turbid, pale yellow liquid. The moisture is estimated by allowing to stand over calcium chloride (not sulphuric acid) in the cold. Nitroglycerine should be practically free from acidity and alkalinity; to test for these, 20 g. is shaken with 50 c.c. of water and the water tested with litmus and if necessary titrated, using methyl orange as indicator.

The nitrogen content is usually determined by the nitrometer method, but the Devarda method may also be used.[5] Another method is to saponify the nitroglycerine with sodium ethylate and reduce to ammonia with a mixture of powdered zinc and iron.[6]

Stability tests are given under *C* (p. 558 *et seq.*).

[1] *Ann. Rep. H.M. Insp. of Expl.*, 1907, 17; *Arms and Expl.*, 1908, **16**, 122; 1909, **17**, 8; *cf.* Naoum, *Chem. Zeit.*, 1924, **48**, 311; Patterson, *Z. ges. Schiess- u. Sprengstoffw.*, 1910, **5**, 14.

[2] Reilly and Rae, *Physico-Chemical Methods*, 1940; *cf.* Gibson and Jacobs, *J. Chem. Soc.*, 1920, **117**, 473.

[3] *J. Chem. Soc.*, 1913, **103**, 1653.

[4] *Chem. Zeit.*, 1932, **56**, 20.

[5] Köhler, Marqueyrol, Jovinet, *Ann. Chim. analyt.*, 1920, (2) **2**, 271; *Mém. Poudres*, 1922, **19**, 356.

[6] Silberrad, Phillips, and Merriman, *J. Soc. Chem. Ind.*, 1906, **25**, 628.

The limit for the heat test of nitroglycerine extracted from dynamite, etc., is fifteen minutes at 160° F. The nitroglycerine must be dry, as moisture prolongs the test. It should be filtered into the test-tube through a dry filter paper, taking care that it does not wet the sides of the tube.

It has been found by Crawford [1] that small quantities of tera-nitromethane and nitrochloromethanes are frequently present in nitroglycerine, and depress the heat test. They may be removed by shaking with sodium sulphite solution.

The melting point is not a good criterion of the purity of nitroglycerine. Nitroglycerine supercools very readily and must be seeded with crystals of the solid substance.[2]

Mixtures of nitroglycerine with tetranitrodiglycerine are tested in general similarly to nitroglycerine. An admixture of 30 per cent. tetranitrodiglycerine lowers the nitrogen percentage to 17·6-17·7. The physical properties of the mixture are not sharply defined; it is a viscous oil of indeterminate freezing point. In its solubilities, etc., it is in general similar to nitroglycerine.

(c) Dinitroglycol

Ethylene glycol dinitrate, $C_2H_4(NO_3)_2$. Mol. wt., 152·0; sp. gr., 1·496 (15°); M.P.,—20°; soluble in 100 parts water, 0·6 at 15°; soluble in organic solvents.

Dinitroglycol is a colourless liquid, less viscous than nitroglycerine. It has a very low freezing point and in admixture with nitroglycerine the freezing point is still further depressed. It is a frequent constituent of non-freezing explosives. It dissolves in most organic solvents, but is sparingly soluble in carbon disulphide.

Dinitroglycol is tested similarly to nitroglycerine. It is, however, considerably more volatile than nitroglycerine and loses weight readily on heating, and even to some extent at ordinary temperature. It should give no residue on evaporating at 50° (absence of nitroglycerine, etc.).

The nitrogen content is almost identical with that of nitroglycerine and does not therefore give any indication of the percentage composition of mixtures.

Marqueyrol and Goutal [3] have given methods for the estimation of dinitroglycol in nitroglycerine. These depend on the action of sulphuric acid and the depression of the freezing point of benzene. Rinkenbach [4] has given a method depending on refraction.

[1] *J. Soc. Chem. Ind.*, 1922, **41**, 321.
[2] Kast, *Z. ges. Schliess- u. Sprengstoffw.*, 1906, **1**, 225.
[3] *Mém. Poudres*, 1921, **19**, 87.
[4] *Ind. Eng. Chem.*, 1927, **19**, 1291.

(d) Dinitrochlorhydrin

Chlorohydrin dinitrate, $CH_2ClCH(NO_3)CH_2NO_3$. Mol. wt., 200·5; M.P., α: +5°, β: +16°; sp. gr., 1·541 at 15°; solubility in 100 parts water, 0·23 at 15°; soluble in organic solvents.

Dinitrochlorhydrin forms a colourless liquid with a slightly aromatic odour. The commercial product is yellow to yellowish-brown. It is less viscous and more volatile than nitroglycerine.

Dinitrochlorhydrin always contains a small proportion of nitro-dichlorhydrin. A chlorine estimation of a mixture in which nitroglycerine is also present does not therefore give definite evidence of the composition. The nitrogen determination also cannot be relied upon, unless the unchlorinated portion of the raw material is known.

The examination includes determination of specific gravity, nitrogen and chlorine content. The nitrogen content of the pure di-nitrochlorhydrin is 13·97 per cent. In practice about 13·80 to 13·85 per cent. is found. The chlorine is estimated by saponification with alcoholic potassium hydroxide (15 per cent.). After boiling for fifteen minutes the liquid is evaporated and the residue heated, then dissolved in water, neutralized with nitric acid, the nitrite oxidized with permanganate, and the chlorine estimated by Volhard's method.

In some cases the refractive index is made use of for mixtures, but the results are not usually very reliable.

(e) Starch Nitrate

Nitrated starch is used in the United States as an ingredient of blasting explosives. The nitration of starch gives nitric esters with about the same nitrogen content as with celluloses. The starch nitrate (often incorrectly designated *nitro*-starch) dissolves readily in acetone and ethyl acetate and to some extent in ether-alcohol. The solutions show a relatively low viscosity. It is much more hygroscopic than cellulose nitrate and is mixed with oils to prevent absorption of water. A partly acetylated starch on nitration gives a less hygroscopic product due to reduction of free hydroxyl groups in the nitrated product.[1]

The nitrogen content is determined by the nitrometer method, or by the method of Schulze-Tiemann. In the former method some difficulty is experienced, as the starch nitrate does not dissolve very readily in the sulphuric acid. It may, however, be dissolved by shaking in a stoppered bottle and then introduced into the nitrometer. In the Schulze-Tiemann method difficulties arise because the granules adhere to the walls of the vessel. Kessler[2] therefore recommends

[1] A bibliography of the starch nitrates is given by Matla, *Chem. Weekblad*, 1936, **33**, 120.
[2] *Z. angew. Chem.*, 1922, **35**, 145.

hydrolysing with potassium hydroxide and reducing the nitrate and nitrite to ammonia with Devarda's alloy.

Carbonates are estimated as in cellulose nitrate. Stability tests are also included. In America the loss of weight at 100° is measured (see Section *C*, VI. (*a*), Sy's method, p. 573). The stability is somewhat poor.[1]

(f) Nitromannite

Mannite hexanitrate, NO_3, $CH_2(CHNO_3)_4CH_2NO_3$. Mol. wt., 452; sp. gr., 1·604; M.P., 112° to 113°; insol. water, slightly sol. cold alcohol, sol. ether and acetone.

This forms a somewhat voluminous white crystalline powder, which should give a clear solution in ether. The pure compound contains 18·58 per cent. of nitrogen and the technical product approaches this value. The stability is somewhat poor and the explosive is expensive. The purity of the compound is best determined by the melting point.

(g) Nitrated Polysaccharides

Recently, in addition to nitrated celluloses, starch nitrate, etc., various nitrated products of other polysaccharides have received attention, *e.g.* nitrated inulin, nitrated lichenin. The following is an example of the preparation of one of these products on a small scale [2]:

Finely powdered lichenin (1 part) was gradually added at room temperature to a mixture (50 parts) of 3 parts by weight of sulphuric acid (sp. gr. 1·84) and 1 part by weight of nitric acid (sp. gr. 1·5). After each addition of lichenin, the nitration mixture was stirred. The lichenin nitrate was separated by decantation, and purified by boiling for a short time first with slightly acid water, then with alkaline tap water, finally with distilled water, and then dried at low temperature. The lichenin nitrate was also separated from the waste acids in another experiment by a modification of the Thomson "displacement process." The product contained 12·4 per cent. nitrogen. $C_{12}H_{15}O_5(NO_3)_5$ requires N = 12·7 per cent.

Lichenin pentanitrate is readily soluble in acetone, ethyl acetate, and amyl acetate, but insoluble in ether, benzene, and water. When gelatinised with a solvent, it gives a product resembling horn. Like nitrocellulose of the same percentage nitrogen composition, it is almost completely soluble in a mixture of ether and alcohol, and decomposes at high temperatures, giving off oxides of nitrogen.

[1] Berl and Bütler, *Z. ges. Schiess- u. Sprengstoffw.*, 1910, 5, 82; Schrimpff, *ibid.*, 1930, 25, 273.

[2] Reilly, Hayes and Drumm, *Sci. Proc. Roy. Dub. Acad.*, 1931, 40, B, 8, 104.

(h) Tetranitropentaerythritol (Penthrit)

Pentaerythritol-tetranitrate, $C(CH_2NO_3)_4$. Mol. wt., 316·0; sp. gr., 1·73 to 1·74; M.P., 140° to 141°; insol. water, slightly sol. in ether, sol. acetone.

Pentaerythritol-tetranitrate should be in the form of fine white crystals and should have no tendency to agglomerate. The technical product melts at 135° to 137°. The pure compound (M.P. 138·5° to 141°) gives a clear solution in warm acetone, but a slight residue of calcium salts is usually found. The compound should be neutral. The nitrogen content of the pure compound is 17·74 per cent.; usually a percentage of 17·3 to 17·4 is found. Other tests include ash, moisture and acidity. The last is determined by dissolving in acetone, reprecipitating with water, filtering and testing the filtrate for sulphuric and nitric acid.[1]

III. Aromatic Nitro-compounds

A number of higher nitro-compounds of benzene derivatives are used for military purposes, *e.g.* trinitrotoluene and trinitrophenol. Mono- and dinitro-compounds are used in industrial explosives. The separation of mixtures of nitro-compounds is somewhat difficult; in some cases steam distillation is of assistance, a partial separation may be effected by solvents, and certain colour reactions are used. Several general tests for the nitro-group have been described. Olivier[2] recommends dissolving in benzene and adding aluminium chloride; nitro-compounds give a red colour. Mulliken and Barker[3] dissolve the nitro-compound in alcohol, add a trace of calcium chloride, reduce with zinc and test for the hydroxylamine group by the silver mirror test. In an alternative method, 3 to 4 drops of the compound are boiled with 2 ml. of a mixture of equal parts of aniline and ortho- and para-toluidine together with 2 ml. of water, 2 ml. of conc. hydrochloric acid and a gram of iron filings. This gives fuchsine, which on pouring into dilute acetic acid gives a red colour. A number of the nitro-compounds give characteristic colours with alkalis and these are of assistance in the identification of the compounds.[4]

For the quantitative estimation the nitrometer method is not in general applicable, though the nitramine group in tetryl responds to this test. The Dumas method may be used under precautions, and the Kjeldahl method is sometimes used for the lower nitro-compounds. Titration methods depending on reduction with stannous chloride are described by Limpricht,[5] Colver and Prideaux[6] and

[1] For stability, see Stettbacher, *Z. ges. Schiess- u. Sprengstoffw.*, 1930, **25**, 278.
[2] *Rec. trav. chim.*, 1918, **37**, 241.
[3] *Amer. Chem. J.*, 1898, **21**, 271.
[4] Copisarow, *Chem. News*, 1914, 247; *Z. anal. Chem.*, 1921, **60**, 239.
[5] *Ber.*, 1878, **11**, 35.
[6] *J. Soc. Chem. Ind.*, 1917, **36**, 480.

Altmann.[1] Reduction with titanous chloride and sulphate is also employed.[2]

The tests which are applied to nitro-compounds usually include setting point, volatile matter, free acid, residues insoluble in organic solvents, and ash. Occasionally special tests for exudation, etc., are specified.

(a) Picric Acid

Trinitrophenol $(NO_2)_3C_6H_2OH$. Mol. wt., 229·0; sp. gr., 1·76; M.P., 121·6°; soluble in 100 parts water, 0·8 at 0°, 6·33 at 100°; soluble in organic solvents.

Picric acid should be of uniform yellow colour and free from visible impurities. It should melt to a yellow or light brown liquid, which should not darken on continued heating. The melt should be practically free from scum or deposit.

Metallic picrates and oxalates should be absent, and other nitro-compounds should be present only in traces. The melting point or setting point carried out on a well-dried sample should be at least 120°. The moisture content is generally limited to 0·1–0·25 per cent., and the ash to 0·05–0·1 per cent.; this should not be of a gritty nature. Impurities insoluble in water should not exceed the ash content by more than 0·05 per cent. The picric acid should be almost completely soluble in benzene. Sulphates are restricted to 0·05–0·1 per cent. (as SO_3). Chlorides and nitrates are sometimes tested for. Absence of lead in any form which might give rise to the formation of lead picrate is of special importance. Lead sulphate is, however, comparatively harmless.

The setting point is determined by allowing the molten acid to cool slowly in a broad air-jacketed test-tube.

The volatile matter is measured by heating for two hours at 100°, or three hours at 80°, or in a vacuum desiccator over sulphuric acid for twenty-four hours.

For the determination of the ash, 10 g. of the picric acid is added in very small quantities to a heated crucible. The temperature is then raised to burn off carbon, and the residue is moistened with nitric acid, then with a little sulphuric acid, and again ignited. An alternative method is to moisten the picric acid with concentrated sulphuric acid and heat it gradually.

Sulphates are determined in the ordinary way. Large excess of barium chloride should be avoided.

For the detection of picrates, the picric acid is extracted with

[1] *J. prakt. Chem.*, 1901, **63**, 370.

[2] Knecht and Hibbert, *Ber.*, 1903, **36**, 1549; 1905, **38**, 3318; and *New Reduction Methods in Volumetric Analysis*, 1910; *cf.* also English, *Ind. Eng. Chem.*, 1920, **12**, 994; Callan, Henderson and Strafford, *J. Soc. Chem. Ind.*, 1920, **39**, 86 T.

benzene, and the residue is examined under the microscope and tested by burning. The benzene residue is also examined for oxalates.

Nitrophenolsulphonic acids may be estimated by melting with excess of sodium carbonate, determining the sulphate formed and subtracting the sulphate originally present.

Picric acid may generally be detected by its intense yellow colour and dyeing properties, also by its bitter taste. It may be extracted from its aqueous solution by ether after acidifying strongly with sulphuric acid. On heating with potassium cyanide and sodium hydroxide to 60°–70°, picric acid gives a blood-red colour. Ammonium sulphide also gives a red colour with picric acid. Potassium ferrocyanide gives on warming a bright blue colour and ferricyanide a red colour, both of these changing to reddish-violet. Copper ammonium sulphate gives a greenish-yellow precipitate. Methylene blue gives a violet precipitate. Picric acid forms a sparingly soluble potassium salt, and gives characteristic compounds with naphthalene and phenanthrene. The picrates of cinchonine, berberine, acridine [1] and nitron [2] are almost insoluble and may be used for the quantitative estimation of picric acid. Picric acid may be titrated with alkali, using phenolphthalein or methyl red as indicator.[3]

Ammonium picrate forms yellow crystals which dissolve readily in water. It should be practically free from insoluble matter (0·2 per cent.) and should not give more than 0·2 per cent. of ash.

Trinitrocresol resembles picric acid in general, but melts at 107° and gives a readily soluble potassium salt.

(b) Dinitrotoluene

$CH_3C_6H_3(NO_2)_2$. Mol. wt., 182 ; M.P., 70·5° ; insol. water, soluble in organic solvents.

A large number of industrial explosives contain dinitrotoluene or trinitrotoluene or mixtures of these. The dinitrotoluene is mainly the 1 . 2 . 4 isomer, but contains some of the other isomers. Different grades of purity are met with ; a good quality material has a setting point of 66° to 68°. It should not smell of mononitrotoluene. The acidity should not exceed 0·1 per cent. and the compound should melt to a transparent yellow liquid. The volatile matter should not exceed 0·25 per cent., and the residue on ignition should not be greater than 0·05 per cent. On dissolving in benzene, the residue should not exceed 0·10 per cent.

[1] Anschutz, *Ber.*, 1884, **17**, 438.

[2] Busch and Blume, *Z. angew. Chem.*, 1908, **21**, 354.

[3] Minovici and Kollo, *J. Chem. Soc., Abstr.*, 1915, **108**, ii. 383.

(c) Trinitrotoluene

$(NO_2)_3C_6H_2CH_3$. Mol. wt., 227·0; sp. gr., 1·68; M.P., 81°; soluble in 100 parts water, 0·02 at 15°, 0·16 at 100°; soluble in organic solvents.

Trinitrotoluene (also known as TNT, trotyl, trinol, etc.) is used as such and also in admixture with ammonium nitrate, etc., in explosives such as amatol, ammonal, sabulite, donarite, etc. This substance is the most important military high explosive.

The pure compound forms pale yellow crystals. The best indicator of the purity is the setting point. At the present time the commercial product is available in a very high degree of purity. The compound must be dry, as the setting point is depressed by water. About 50 g. of the trinitrotoluene is melted in a dish at 100°; any drops of water are removed by means of a filter paper, and the heating is continued for two hours with stirring. The molten material is poured into a broad test tube fitted with a cork and thermometer. This tube is fitted into a wider tube leaving an air space of about 5 mm., and the double tube is placed in a vessel of about 1 litre capacity. The trinitrotoluene is stirred during cooling, and the maximum temperature after crystallization has set in is observed. For crude trinitrotoluene a setting point of about 76° is usually required, and for purified trinitrotoluene 80° or sometimes slightly higher. The molten trinitrotoluene should be of a medium brown colour and should not darken on continued heating at 100°. It should be clear and should not deposit any particles of grit.

A benzene solution of the trinitrotoluene should contain only traces of insoluble organic compounds (0·1 to 0·2 per cent.).

For the estimation of the ash, 5 g. of the substance is moistened with 2 ml. sulphuric acid and burnt off. The residue is moistened with a little nitric acid, then with sulphuric acid and reheated. The ash should not exceed 0·05 per cent.

The volatile matter may be estimated by the " dish and cone " method (see Smokeless Powder, p. 538). It is also sometimes determined by drying on a watch glass in a vacuum at ordinary temperature. Limits of 0·1 to 0·25 per cent. are usually specified.

For the determination of acidity, the trinitrotoluene is melted under water with stirring. The water is decanted and the extraction repeated twice. The water extract is tested either with litmus or by titration to phenolphthalein. The acid may include sulphuric and nitric acid, which are sometimes tested for separately, and organic acids (nitrocresols, etc.).

Tetranitromethane in crude trinitrotoluene may be estimated by reduction of hydrazine in alkaline solution to nitrogen.[1]

[1] Baillie, Macbeth, and Maxwell, *J. Chem. Soc.*, 1920, **117**, 880.

Heavy metals are sometimes tested for, and occasionally the nitrogen content is estimated (by the Dumas method).

The methods of testing trinitrotoluene in America are given by Stevens,[1] and those in Germany by Kast and Metz.[2]

A method for the estimation of trinitrotoluene by means of nitrosodimethylaniline is given by Secareanu.[3] For the estimation of trinitrotoluene in presence of tetryl, Taylor and Rinkenbach[4] give a method depending on the difference of solubility in carbon tetrachloride.

"Liquid trinitrotoluene" is a mixture of isomeric trinitrotoluenes with some dinitrotoluene which forms a by-product in the purification of trinitrotoluene by crystallization or centrifuging. It has a limited use in commercial explosives. Its melting point and other properties are very indefinite.

(d) Dinitrobenzene

$C_6H_4(NO_2)_2$. Mol. wt., 168; M.P., 90°; insol. water; soluble in organic solvents.

Dinitrobenzene is but little used. It is objectionable on account of its poisonous properties. The main ingredient is the meta-derivative, but the other isomers are also present, and the commercial product may give a setting point as low as 80°. It should be free from mono-nitrobenzene, which can be recognized by its smell.

(e) Trinitrobenzene

$C_6H_3(NO_2)_3$. Mol. wt., 213; M.P., 122°; insol. water; soluble in organic solvents.

Trinitrobenzene is also but little used. It forms additive compounds with amines and with naphthalene. It gives an intense red colour with alkalis in presence of alcohol.

(f) Nitronaphthalenes

These are used in various mixed explosives. They are usually met with in an impure form.

Mononitronaphthalene. The commercial product consists mainly of the alpha-compound. The pure compound melts at 61°. The commercial product should have a melting point of at least 56°. It boils at 304°. It is tested in the usual way for absence of acidity, insoluble matter, etc.

Dinitronaphthalene. This is a mixture of the 1·5-isomer (M.P. 217°) and the 1·8-isomer (M.P. 170°). It has an indefinite melting

[1] *Ind. Eng. Chem.*, 1917, 9, 801.
[2] *Chem. Unters. d. Spreng- u. Zündstoffe.*
[3] *Ber.*, 1931, 64, B, 834.
[4] *Ind. Eng. Chem.*, 1923, 15, 280.

point, usually about 135° to 140°. It forms a dirty yellow to red brown crystalline powder. It gives a pink colour with alcoholic ammonia.

Trinitronaphthalene. This was used to some extent during the War in admixture with picric acid, etc. It is a mixture of various isomers and has no definite melting point. The melting points of the individual constituents are 1 : 3 : 8 (218°), 1 : 2 : 5 (113°), 1 : 3 : 5 (122°), 1 : 4 : 5 (154°). Some dinitronaphthalene is also present. The nitrogen percentage gives some indication of the proportion of trinitro-compound.

(g) Tetryl

Trinitrophenyl methyl nitramine $(NO_2)_3C_6H_2N(CH_3)NO_2$. Mol. wt., 287; sp. gr., 1·725; M.P., 131°; insol. water; soluble in organic solvents.

Tetryl forms a yellow crystalline solid. It should melt at 129° or above. It decomposes somewhat readily when molten and the setting point cannot be satisfactorily measured. It should leave only a trace of residue when dissolved in acetone and should be practically free from acid. In some countries a distinction is drawn between surface acid and that which is found by dissolving the tetryl in an organic solvent and adding water. Tetryl is much less soluble in carbon tetrachloride than trinitrotoluene; this is made use of for the separation of the nitro-compounds. Melting-point diagrams are also made use of to estimate the composition of such mixtures.[1]

The nitramine nitrogen may be estimated by the nitrometer method.[2] Tetryl is less stable than the majority of nitro-compounds. The stability may be estimated by the evolution of gas on heating in a vacuum (see p. 575).

(h) Other Nitro-compounds

Dinitrophenol $(NO_2)_2C_6H_3OH$. The pure 1 : 2 : 4 compound melts at 114°, commercial samples usually at about 110° to 112°. It has acid properties and forms salts. It should dissolve completely in cold dilute sodium hydroxide solution and in benzene, and should not contain more than 0·1 per cent. of organic chlorine. It should be free from lead. It is somewhat volatile in steam and can be separated from picric acid by steam distillation, though not very readily. The dinitrophenol in a mixture with picric acid may be estimated by bromination.

Trinitroanisole $(NO_2)_3C_6H_2OCH_3$. This is the methyl ester of picric acid and as such can be hydrolysed to picric acid by warm

[1] Taylor and Rinkenbach, *Ind. Eng. Chem.*, 1923, **15**, 280, 1070.

[2] Lehmstedt, *Z. angew. Chem.*, 1926, **39**, 379; Desvergnes, *Ann. Chim. anal.*, 1926, i., **8**, 353.

alkalis. The pure substance melts at 68°, the commercial product at about 65°. It should be free from mineral acids and from picrates.

Trinitroresorcinol (Styphnic acid) $(NO_2)_3C_6H(OH)_2$. This is an acid somewhat similar to picric acid in its general properties. It melts at 175·5°.

Trinitrochlorobenzene $(NO_2)_3C_6H_2Cl$. This has been very little used as an explosive, but serves for the preparation of other trinitro-compounds. It melts at 83°. The chlorine is very reactive and is readily replaced by the amino- or hydroxy-group.

Hexanitrodiphenylamine $(NO_2)_3C_6H_2 . NHC_6H_2(NO_2)_3$. This compound melts at about 230°, but undergoes decomposition below the melting point. It is almost insoluble in most solvents, but dissolves in a mixture of acetone and pyridine, and the solution should leave very little insoluble residue. The compound has acid properties and forms salts of various metals.

2-4-6 *Trinitrometaxylene* $(CH_3)_2C_6H(NO_2)_3$. On nitration of commercial xylene, this product is obtained in admixture with *o*- and *p*-nitrated xylenes, especially dinitro-derivatives. The melting point of the crude explosive is 182°, and to lower the melting point the product is mixed with trotyl.

Hexanitrodiphenylsulphide $(NO_2)_3C_6H_2SC_6H_2(NO_2)_3$. The pure substance melts at 233°, the commercial product at about 225°. It is tested as usual for acids and other impurities.

Tetranitroaniline. Yellow crystals of M.P. 216°. The methods of testing are given by Flürscheim.[1]

IV. Smokeless Powders

The composition of smokeless powders varies greatly, but they contain in general nitrocellulose, either completely or partially gelatinized. The completely gelatinized powders have a more or less horny structure; the partially gelatinized powders are porous, and can be comparatively easily broken down to powder. Many smokeless powders contain nitroglycerine, and most contain stabilizers.

Preparation of Sample. Gelatinized powders are ground in a mill of the coffee-mill type (see Abel Heat Test, p. 559). A small portion is passed through and discarded, and the main sample is passed through the sieves as used for the heat test. For general analysis, the material which passes through holes of 0·032 inch diameter is taken.

Some powders in the form of small flakes do not require grinding. Particles of iron may be removed from ground powders by a magnet. For the quantitative analysis the powder is dried at 60° to 70° to

[1] *J. Soc. Chem. Ind.*, 1921, 40, 97 T.

remove the solvent. Nitroglycerine powders should not be warmed for more than an hour at 60°. Alternatively, the volatile matter may be determined on a separate portion of the ground powder.

Qualitative Analysis

The nature of the gelatinizing solvent can generally be detected by its smell. The powder should then be tested to ascertain whether it is a nitrocellulose powder or whether it contains nitroglycerine. It is digested for a considerable time with ether, decanted, and the solution allowed to evaporate in a dish. If a minute quantity of the liquid is absorbed on a piece of filter paper and struck on an anvil, an explosion occurs if the liquid be pure nitroglycerine. Apart from nitroglycerine, ether extracts stabilizers, nitro-compounds, etc. Camphor is detectable by its smell. Diphenylamine is recognized by the blue colour which it gives with sulphuric and nitric acids. On heating a solution of diphenylamine in 95 per cent. alcohol with a few drops of chlorine water, a green coloration is formed, changing slowly to dark violet on keeping or warming.[1] Mineral jelly may be separated from nitroglycerine by boiling with 80 per cent. methyl alcohol. Substituted ureas and urethanes are also sometimes met with. The aqueous extract is examined for salts, and the ash is also tested.

Quantitative Analysis

Volatile Matter.—This includes the gelatinizing solvent and water. In absence of volatile ingredients, such as nitroglycerine, the weighed ground powder may be dried by heating, and then reweighed. Temperatures of 65° to 100° are employed. It is of importance to avoid loss of volatile matter of the ground powder in the cold before weighing. For this reason the powder should not be too finely ground. Some heating takes place during the grinding. In some cases the powder is not ground, but is cut up into pieces, dissolved in ether-alcohol, reprecipitated by water, evaporated and dried in a vacuum at 50° or by heating to 95°-100°. The loss of weight, corrected for any residues in the solvent represents the volatile matter. The object of this procedure is to avoid initial losses of solvent. If a slightly volatile ingredient be present, the estimation may be made by drying at ordinary temperature in a vacuum.

In powders containing nitroglycerine, the volatility of the latter exercises a disturbing effect. To prevent escape of nitroglycerine, the apparatus shown in Fig. 120 is used. This was devised by Dupré[2] and improved by Marshall.[3] It consists of an aluminium dish A

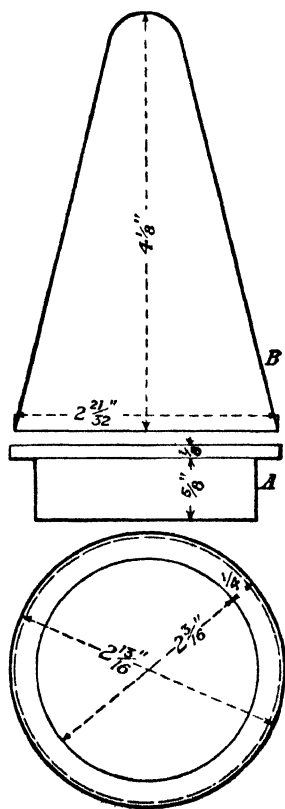
[1] Desvergnes, *Ann. Chim. analyt.*, 1929 (ii), **11**, 1.
[2] *Chem. Zeit.*, 1901, **25**, 540. [3] *J. Soc. Chem. Ind.*, 1904, **23**, 154.

and a conical glass-cover B, the whole apparatus weighing about 40 g. The ends of the sticks of powder are discarded and it is then ground as for the heat test. This should occupy one and a half to two minutes. Approximately 5 g. is weighed out into the dish, which is then covered with the cone, the whole accurately weighed and heated on an iron plate resting on a water bath. After three hours the apparatus is allowed to cool for half an hour in a desiccator, and weighed. The cone should rest closely on the rim of the dish to prevent loss of nitroglycerine. The nitroglycerine condenses completely on the glass cone. Separate determinations of water and organic solvent are not usually undertaken. Distillation with xylene has been used [1] for the estimation of water. Dupré [2] gave a method depending upon the reaction between water and calcium carbide. Pieroni [3] proposed to subject the powder to steam distillation and estimate acetone in the distillate by conversion to iodoform. A review of the method is given by Becker and Dittmar.[4]

FIG. 120.

Chemical Analysis.—The powder is first extracted in a Soxhlet or other extraction apparatus to separate the nitroglycerine, etc. Pure dry ether should be used; sometimes a little chloroform (10 per cent.) is mixed with the ether to prevent solution of nitrocellulose. The solution is carefully evaporated and the flask is placed on a hot-plate surmounted by a sheet of uralite with holes which do not permit the flask to touch the hot-plate. From time to time the flask is removed and air, at ordinary temperature, is blown through it. This is continued until the weight becomes constant. The nitroglycerine, etc., may also be dried in a vacuum over calcium chloride.

A *nitrogen* determination may then be made by the nitrometer method. Care should be taken in introducing a solution of the substances in concentrated sulphuric acid into the nitrometer, as ether peroxide may give rise to heating and explosion in the bulb.[5]

It is to be observed that the nitrogen determination may be

[1] *Reichsanstalt*, *Ann. Rep.* IV., 1924-25, 100.
[2] *Analyst*, 1906, **31**, 213.
[3] *Atti R. Accad. Lincei*, 1918, **27**, ii. 52.
[4] *Z. ges. Schiess- u. Sprengstoffw.*, 1934, **29**, 327.
[5] *Cf.* p. 545.

disturbed by mononitrobenzene derivatives, as these are partially nitrated to dinitro-derivatives. Diphenylamine and other stabilizers also affect the results. As the Schulze-Tiemann method is rendered inaccurate by the volatility of the nitroglycerine, it has been proposed to hydrolyse a weighed quantity of the residue with alcoholic potassium hydroxide and estimate the nitrogen by ferrous chloride and hydrochloric acid.

In extracting nitroglycerine with ether and evaporating as above, slight losses of nitroglycerine occur by reason of its volatility. For this reason the nitroglycerine is sometimes estimated by difference. Silberrad, Phillips, and Merriman [1] described a method in which the ether-extract is boiled with sodium ethylate to saponify the nitroglycerine, and the nitrogen reduced to ammonia by powdered zinc and iron.

Mineral jelly or *paraffin* may be separated from nitroglycerine by boiling with 80 per cent. methyl alcohol.[2] This dissolves the nitroglycerine. The solution is filtered and the insoluble portion dissolved in ether, evaporated and weighed. Alternatively the nitroglycerine may be removed by saponification with alcoholic potassium hydroxide, and the solution diluted with water and extracted with ether.

For the *separation of nitroglycerine from nitroaromatic compounds*, Hyde [3] gives a method depending on extraction with carbon disulphide and 65 per cent. aqueous acetic acid. Dickson and Easterbrook [4] recommend separating nitroglycerine from nitro-compounds by dissolving the mixture in methyl alcohol and destroying the nitroglycerine by ferrous chloride solution, after which the solution is extracted with ether. Lutri [5] hydrolyses the nitroglycerine with 20 per cent. sulphuric acid and extracts the nitro-compounds with benzene. For the determination of dinitrotoluene, etc., used as surface coatings of powders, see Taylor and Rinkenbach.[6]

Camphor may be estimated according to Foerster [7] by heating the powder with water on a water-bath and adding sodium hydroxide solution gradually. The heating is continued until the structure of the powder is destroyed. The camphor is distilled over with some of the water into a receiver of special design, in which it is treated with a known quantity of benzene, and natural camphor determined by means of a polarimeter. A gravimetric method is described by Vieth and Bilhuber,[8] in which the powder is hydrolysed as above and the camphor distilled over into a receiver containing ether. After

[1] *J. Soc. Chem. Ind.*, 1906, **25**, 628. [2] Marshall, *Explosives*, vol. ii., p. 713.
[3] *Int. Congr. Appl. Chem.* VIII., 1912, **4**, 69; *J. Amer. Chem. Soc.*, 1913, **35**, 1173.
[4] *Analyst*, 1922, **47**, 112. [5] *Giorn. Chim. Ind. Ital. Appl.*, 1920, **2**, 557.
[6] *U.S. Bur. Mines, Bull.* **219**, 1923, 152. [7] *Ber.*, 1890, **23**, 2981.
[8] *J. Amer. Pharm. Assoc.*, 1924, **13**, 636.

repeated extractions with ether, the ethereal solution is dried with calcium chloride and a portion is evaporated.

For the estimation of *diphenylamine* the powder may be saponified as above, and then distilled until all the diphenylamine has passed over. The distillate is extracted with ether, which is separated, dried with calcium chloride and evaporated. The diphenylamine may also be estimated by conversion to tetrabromo-diphenylamine. For this purpose the ethereal solution is evaporated with alcohol, and excess of bromine is added to the alcoholic solution with stirring. The tetrabromo-diphenylamine separates out, and the supernatant liquor should be clear and should smell distinctly of bromine. Water is added and the whole is boiled to remove alcohol and bromine. The bromine compound is filtered off, washed with warm water and dried in a steam oven.[1] The bromination may also be effected by potassium bromate and bromide in acid solution. Other methods of estimation are given by Cook.[2] Urea derivatives may also be present. Diphenylurea (asymm.) is hydrolysed by strong sodium hydroxide solution and the resultant diphenylamine is estimated.

Centralite is converted to a dibromo-derivative on bromination and may be estimated volumetrically by the bromide-bromate method. Levenson[3] brominates in alcoholic solution. Ellington and Beard[4] use a carbon tetrachloride solution to avoid any interaction between the bromine and the solvent. The reagents consist of (1) 0·2 *N* bromide-bromate containing 5·568 g. potassium bromate and 30 g. potassium bromide per litre, and (2) 0·2 *N* thiosulphate. The propellant is extracted with ether in a Soxhlet using a 200 ml. reaction bottle as receiver. The ether is then distilled off and the last traces are removed by a current of air. After cooling, 50 ml. of pure carbon tetrachloride is added and the bottle shaken, whereupon 50 ml. of bromide-bromate solution and 10 ml. conc. hydrochloric acid are added. The bottle is shaken for five minutes and 20 ml. of 15 per cent. potassium iodide added. After vigorous shaking, the solution is titrated with thiosulphate. A blank test is included.

A separation of diphenylamine from centralite may be effected by precipitation of tetrabromodiphenylamine in aqueous alcohol, in which dibromocentralite is soluble.[5]

After the extraction of all soluble ingredients by means of solvents, the *nitrocellulose* remains behind, together with any mineral matter,

[1] Dreger, *Z. ges. Schiess- u. Sprengstoffw.*, 1909, **4**, 123; Ryan and O'Riordan, *Proc. Roy. Irish Acad.*, 1919, **34**, B, 218; Bresser, *Z. ges. Schiess- u. Sprengstoffw.*, 1935, **30**, 42.

[2] *Ind. Eng. Chem.* (*Anal.*), 1935, **7**, 250.

[3] *Ibid.*, 1930, **2**, 246.

[4] *J. Soc. Chem. Ind.*, 1931, **50**, 151 T.

[5] *Reichsanstalt, Ann. Rept.* VI., 1927, 133; Bresser, *Nitrocellulose*, 1931, **2**, 210; Desmaroux, *Mém. Poudres*, 1932, **24**, 289: Becker and Hunold, *Z. ges. Schiess- u. Spreng-stoffw.*, 1933, **28**, 233, 284.

and may be dried and weighed. If necessary the nitrocellulose may be dissolved in acetone (1 litre of acetone to 10 g. of propellant). After allowing to stand, the liquid is decanted and a further portion of acetone added. This is shaken, allowed to stand and decanted. The residue is filtered and the combined acetone solutions are poured into 5 volumes of 1 per cent. aqueous calcium chloride solution. The acetone is boiled off and the precipitated nitrocellulose is collected, washed with hot water, dried and weighed. Chloroform is sometimes used to precipitate the nitrocellulose. A nitrogen determination is made on the nitrocellulose. The nitrogen is also determined in the original powder. It is to be observed that substances such as diphenylamine, camphor, naphthalene, resins, etc., have a disturbing influence on the results of the nitrogen determination. The matter insoluble in acetone may contain carbonates, nitrates, graphite, cellulose, starch and mechanical impurities.

The *mineral matter* (ash) in smokeless powders is estimated by heating carefully in a porcelain dish with a few cubic centimetres of fuming nitric acid on a water bath and evaporating. The residue is then incinerated. Sand may be estimated in the ash by dissolving out the other constituents with warm hydrochloric acid. The ash is also examined for salts of potassium, sodium, calcium, barium and magnesium.

Mercury is estimated as in nitrocellulose. Dupré[1] describes the application of the spectroscopic method to smokeless powders. Hehner[2] gives a method based on precipitation of the mercury by copper and conversion to mercuric iodide. Berkhout[3] gives a method depending on the estimation as metallic mercury.

V. Industrial Blasting Explosives

The explosives in use for mining, etc., consist of mixtures of a wide range of oxidizing and reducing substances, and the methods of separation can be given only in outline.[4] Some explosives are in the form of powder, others in gelatinous form; in the latter case the gelatinous mass should be cut into thin shavings with a horn spatula to facilitate extraction. Before the examination it is advisable to satisfy oneself that the explosive is reasonably safe to handle. A small portion should be rubbed vigorously in a porcelain mortar with a porcelain pestle.

[1] *Arms and Explosives*, 1908, **16**, 122. [2] *Ibid.*, 1909, **17**, 9.

[3] *Z. ges. Schiess- u. Sprengstoffw.*, 1912, **7**, 67.

[4] For fuller details see Scott, *Standard Methods of Chemical Analysis*, vol. ii., p. 1372, and *U.S. Bur. Mines, Bulletins* **51**, **96**, **219**, and *Tech. Paper* 78.

Qualitative Examination

Some indications can be obtained by the smell and appearance. Nitroglycol and dinitrochlorhydrin have a faint odour. Some nitro-bodies such as mononitrotoluene have a distinctive smell. Charcoal and aluminium are distinctive in appearance.

A small sample should be extracted repeatedly with pure dry ether. After digesting and allowing to stand the ethereal solution is filtered off and allowed to evaporate in a warm place. A small drop of the residual liquid is absorbed on a piece of filter paper and hammered on an anvil. Nitroglycerine explodes with a sharp crack. Nitroglycol and dinitrochlorhydrin behave similarly. Nitric esters give off oxides of nitrogen on gently warming with ferrous chloride and hydrochloric acid. The specific gravity may also be made use of if ether-soluble substances other than these esters are absent.

Camphor remains dissolved in the nitroglycerine and gives a distinctive odour. It can be extracted by carbon disulphide. Sulphur, paraffin wax and resins separate out from the nitroglycerine. Sulphur crystals may be collected and burnt, giving an odour of sulphur dioxide. Paraffin wax is insoluble in cold alcohol. Resins may be separated from nitroglycerine by means of 65 to 70 per cent. acetic acid in which they are insoluble. They can be saponified by boiling with soda solution, and are reprecipitated by acid.

Some aromatic nitro-compounds crystallize out from the nitroglycerine ; in certain cases a separation may be effected by extracting the nitroglycerine with 90 per cent. alcohol, in which higher nitro-compounds are sparingly soluble. The nitroglycerine may also be dissolved in 65 per cent. acetic acid, and the nitro-compounds extracted with carbon disulphide.

The residue from the extraction with ether may contain salts, kieselguhr, charcoal, wood meal, nitrocellulose and some undissolved sulphur. The salts are identified by the ordinary reactions ; most of them are extractable by water. Carbonates are dissolved by dilute hydrochloric acid with evolution of carbon dioxide. Collodion may be dissolved in ether-alcohol and gun-cotton in ethyl acetate or acetone. The residual ingredients may be identified to some extent microscopically. Starch is detected by the iodine reaction. Wood meal and charcoal may be removed by ignition, leaving such ingredients as kieselguhr, talc, etc.

In some cases salts may be separated by means of their difference in specific gravity, using heavy liquids such as chloroform and bromoform.[1]

[1] *U.S. Bur. Mines, Tech. Paper* 78.

The following list gives the specific gravities of the commoner salts which may be present :—

Salt.	Sp. Gr.	Salt.	Sp. Gr.
Ammonium alum (cryst.)	1·62	Manganese dioxide	5·03
,, chloride	1·52	Potassium alum	1·75
,, nitrate	1·73	,, chlorate	2·34
,, perchlorate	1·87	,, chloride	1·99
,, sulphate	1·77	,, perchlorate	2·52
Barium nitrate	3·23	,, sulphate	2·66
Calcium carbonate (precip.)	2·72	Sodium chloride	2·17
,, sulphate (anhydr.)	2·97	,, nitrate	2·26
,, ,, (hydrated)	2·32	,, sulphate (anhydr.)	2·66
Magnesium carbonate	3·04	,, ,, (cryst.)	1·46
,, sulphate (cryst.)	1·68		
,, ,, (anhydr.)	2·65		

In some cases the analysis can be simplified. Thus powdered explosives (ammonium nitrate and chlorate explosives) may be extracted directly with water to remove soluble salts, and the insoluble constituents may be filtered off and identified. Petroleum or mineral oil may separate out from some chlorate explosives. Wood meal remains in suspension. Trinitrotoluene is best extracted with acetone. Aluminium is easily recognizable. Calcium silicide remains behind as a black powder, and evolves silicon hydride on addition of hydrochloric acid. Paraffin wax separates from nitro-compounds on melting and forms a surface layer. Naphthalene is detectable by its smell. Such explosives may also contain small percentages of nitroglycerine.

Quantitative Analysis

In the analysis of nitroglycerine compounds, care should be taken to obtain a thoroughly well-mixed sample, as nitroglycerine may segregate. In sampling, the ends of cartridges should be discarded.

Moisture. This may be determined by evacuation over calcium chloride for twenty-four hours. When nitroglycerine, dinitroglycol, nitrobenzene, or nitrotoluene are present, the method given under Smokeless Powders (p. 538) may be used.

The hygroscopicity is sometimes of importance. It is determined by spreading a weighed quantity of the material on a flat dish, which is then placed under a bell jar over water. The increase in weight is determined at intervals. A control test on an explosive or other material of known hygroscopicity must be included, as the absorption of moisture is affected by the temperature. Hygroscopicity tests may also be carried out on cartridges.

Extraction. The explosive is extracted with pure dry ether in a Soxhlet extractor or a Gooch crucible (preferably in a continuous

extraction apparatus). Condensation of water is to be avoided, as this would lead to solution of water-soluble salts. The ether extract, which contains nitroglycerine and allied substances, nitrobenzene and its derivatives, sulphur, oils, mineral jelly, paraffin wax and resins, is allowed to evaporate at about 40° to 45°, taking care to avoid loss of nitroglycerine, etc. Special care should be taken to avoid loss if nitroglycol be present. The evaporation is continued until the weight is constant.

If the nitroglycerine is suspected to contain compounds such as dinitrochlorhydrin, it may be examined by specific gravity, nitrogen content, chlorine content, refractive index. Nitrosugars increase the viscosity and lower the nitrogen content.[1] Hoffman and Hawse give a polarimetric method [2] for nitrosugars.

Tetranitrodiglycerine lowers the nitrogen content of nitroglycerine and is much less readily soluble in 65 per cent. acetic acid. It is also much more viscous than nitroglycerine.

With reference to the nitrogen determination in the nitrometer, it is to be observed that impure ether containing peroxides may give rise to explosions on mixing the extracted substances with sulphuric acid [3] and under other conditions.

It is advisable to mix a small quantity of the extract with sulphuric acid to ascertain whether heat is evolved, and if so, the weighed quantity should be first mixed with sulphuric acid of moderate strength, cooling with ice. Strong sulphuric acid is then added slowly with similar cooling.

Mononitrobenzene and mononitrotoluene give rise to errors in the nitrogen determination, but higher nitro-compounds do not affect it. Naphthalene, diphenylamine, centralite, etc., disturb the nitrogen estimation.

Becker [4] gives a volumetric method for the estimation of nitroglycerine. A solution in acetic acid is boiled with ferrous chloride and hydrochloric acid, and the ferric salt is titrated with titanous chloride, using ammonium thiocyanate as indicator. This is also applicable to dinitroglycol.

Paraffin wax separates out from the nitroglycerine when the ether is evaporated off. It is pressed between filter papers and identified by its form and melting point. To determine its quantity the extract is melted and separated in a warmed separating funnel. Resin may be saponified by hot soda, reprecipitated with acid and weighed, or may be titrated with alcoholic potassium hydroxide, using phenolphthalein as indicator.

[1] *Cf.* Naoum, *Nitroglycerine*. [2] *J. Amer. Chem. Soc.*, 1919, **41**, 235.
[3] Witt, *Z. ges. Schiess- u. Sprengstoffw.*, 1920, **15**, 145; *cf.* Robertson, *Chem. and Ind.*, 1933, 274. [4] *Ind. Eng. Chem.* (*Anal.*), 1933, **5**, 152.

The separation of nitro-compounds, camphor, diphenylamine, etc., from nitroglycerine is dealt with under Smokeless Powders (p. 540).

It is sometimes found convenient to remove the whole of the nitroglycerine by heating for several hours with alcoholic potassium hydroxide. Water and ether are then added, and the mixture shaken in a separating funnel. The ethereal solution is evaporated, and the residue consisting of paraffin, mineral jelly or mineral oils, is weighed. The aqueous solution is acidified with hydrochloric acid and bromine is added to oxidize any sulphur. Any separated resin is filtered off and weighed, and sulphur is determined in the filtrate as barium sulphate. Sulphur may also be separated from nitroglycerine by 65 to 70 per cent. acetic acid.

Material Insoluble in Ether. This is dried at a moderate temperature and carefully transferred to a glass dish. It is then further dried at 80° to 90°, or if ammonium nitrate is present, at 70°. If it is in the form of an agglomerated mass, it should be roughly subdivided before drying. Sulphur, if present, may be extracted with carbon disulphide. The residue is then extracted with successive small quantities of water. Warming is sometimes necessary, particularly for the extraction of potassium perchlorate. On the other hand, if aluminium and ammonium nitrate are present, warming must be avoided, or interaction may occur. In addition to salts, the aqueous extract may include soluble matter from wood meal, which may contain as much as 3 per cent. of soluble substances.

Acids resulting from the decomposition of nitroglycerine may form soluble salts by interaction with calcium carbonate, etc. The various salts are estimated by the usual analytical methods. If perchlorates or other salts containing chlorine are present in conjunction with ammonium salts it is not permissible to remove the ammonium salts by direct heating, as this may lead to losses of chlorine. The residue insoluble in water is extracted with dilute hydrochloric acid to dissolve calcium carbonate, magnesia, zinc oxide and metals. If starch is present it should be hydrolysed by boiling with dilute acid.

The residue remaining insoluble in dilute acid may contain insoluble salts, kieselguhr, wood meal, etc. If nitrocellulose is present, the residue is shaken with ether-alcohol to determine the collodion. The ether-alcohol solution is allowed to settle, and an aliquot portion is withdrawn and evaporated. Gun-cotton, if present, is dissolved in acetone, and the solution evaporated. Acetone dissolves certain constituents of wood meal; errors due to this may be avoided by evaporating the acetone solution to 20-25 ml. and diluting with 100 ml. of hot water, which precipitates the nitrocellulose. The residue is washed several times with the solvent and finally dried

and weighed. It is thus also possible to determine the nitrocellulose by difference.

The insoluble residue may contain charcoal and other carbonaceous matter such as wood meal, etc. These are removed by incineration, and the residual ash contains mineral matter such as kieselguhr.

Nitrostarch is somewhat soluble in ordinary ether containing small quantities of alcohol. For this reason petroleum ether is sometimes used to extract oils, resins and sulphur. The insoluble portion is extracted with water to remove soluble salts and the nitrostarch is then separated from insoluble matter by means of acetone.

In some cases the analysis can be shortened (ammonites, chloratites). A weighed quantity is digested with acetone which readily dissolves nitro-compounds, nitroglycerine and hydrocarbons. The insoluble residue is further tested as above, the salts being extracted with water, and the insoluble residue examined for wood meal, charcoal, aluminium, silicides and mineral matter.

VI. Initiators

(a) Mercury Fulminate

$HgC_2N_2O_2$. Mol. wt., 284·6; sp. gr., 4·42; soluble in 100 parts water, 0·07 at 12°, 0·77 at 100°.

Mercury fulminate forms a white to greyish-brown crystalline powder. It is still the most important initiatory explosive. It is very sensitive to shock or friction and must be handled with great care. Goggles should be worn and should be tested beforehand to ensure their resistance to explosive shock. On heating, it explodes at about 150° to 160°, but may explode on more prolonged heating at 100°. The influence of heat in a vacuum on mercury fulminate under various conditions has been exhaustively investigated by Farmer.[1] Mercury fulminate is insoluble in most organic solvents, but dissolves with decomposition or formation of double compounds in ammonia, iodides, cyanides, thiocyanides, thiosulphates, pyridine, etc.

Mercury fulminate should be at least 98 per cent. pure. It should be neutral, practically free from oxalates, chlorides and metals other than mercury.

The moisture is determined by drying over calcium chloride in a desiccator at ordinary temperature and pressure.

In the determination of the insoluble matter the solvent used may be either pyridine, or an aqueous solution of sodium thiosulphate or

[1] *J. Chem. Soc.*, 1923, **122**, 174.

potassium cyanide. The residue should be carefully dried to avoid loss of mercury by volatilization.

Free mercury may sometimes be detected as tiny globules. A more sensitive test is to warm the fulminate in a test-tube in which a strip of gold leaf is suspended. Metallic mercury shows itself by the formation of spots of amalgam on the gold leaf. For the quantitative estimation, the residue insoluble in pyridine is treated on a filter with a solution of 3 g. potassium iodide and 6 g. sodium thiosulphate in 50 ml. water. This converts any organic mercury compounds to mercuric iodide, which is soluble in thiosulphate. The insoluble matter is dried at 80° to 90° and weighed. This is taken as mercury.[1] Nicolardot and Boudet [2] shake the fulminate with a 5 per cent. solution of ammonium hydrosulphite and report the residue as metallic mercury.

The fulminate value is best determined by the method of Brownsdon.[3] For the determination, 0·3 of the sample is wetted with about 5 ml. of water, and 50 ml. of a solution containing 6 per cent. KI and 2·5 per cent. $Na_2S_2O_3$ (cryst.) is added. The mixture is shaken for about a minute and then neutralized to methyl orange with *N*/10 HCl. The solution and titration should not occupy more than about three minutes as the titre alters rapidly. For the calculation 4HCl is equivalent to $HgC_2N_2O_2$.

The total mercury may be estimated, if required, by precipitation with ammonium sulphide.[4] Losanitsch[5] described an electrolytic method.

Oxalates are estimated by dissolving the fulminate in ammonia, precipitating with ammonium sulphide and determining the oxalate in the filtrate. Alternatively the fulminate may be dissolved in 20 per cent. ammonia and acetic acid added to precipitate most of the fulminate. The oxalate is then determined in the filtrate.[6] According to Rathsburg, mercury fulminate should not decolorize *N*/50 permanganate. Heaven [7] gives a general survey of the testing of mercury fulminate.

(b) Lead Azide

$Pb(N_3)_2$. Mol. wt., 291; sp. gr., 4·80; soluble in 100 parts water, 0·03 at 18°, 0·09 at 80°; sparingly soluble in organic solvents.

Among the initiating explosives lead azide is second in order of importance. It forms fine white crystals, but these tend to increase in size in contact with water and may explode spontaneously. On heating it explodes at 320° to 340°.

[1] *U.S. Bur. Mines, Bull.* **219**, 63.

[2] *Ann. Chim. analyt.*, 1918, **23**, 206.

[3] *Chem. News*, 1904, **89**, 303; *cf.* Philip, *Z. ges. Schiess- u. Sprengstoffw.*, 1912, **7**, 109, 156, 180, 198, 221; Taylor and Rinkenbach, *U.S. Bur. Mines, Bull.* **219**, 1923, 62.

[4] Rose, *Pogg. Ann.*, 1860, **110**, 529.

[5] *Monatsh.*, 1904, **35**, 307; *cf.* Langhans, *Z. ges. Schiess- u. Sprengstoffw.*, 1922, **17**, 141.

[6] Rathsburg, *Ber.*, 1921, **54**, 3185.

[7] *J. Soc. Chem. Ind.*, 1918, **37**, 143 T.

The content of lead azide should be at least 95 to 97 per cent. Usually a little basic azide is present, and this is sometimes preferred, as it is stated to render the material safer. Metals other than lead should be present only in traces. The lead azide should dissolve practically completely in dilute nitric acid. It should be free from acid.

The moisture is determined by drying over calcium chloride or sulphuric acid.

The total lead content may be estimated by evaporating with sulphuric acid on a water bath, and then gradually heating more strongly.[1]

The azide value may be determined by shaking with dilute nitric acid until dissolved and precipitating as silver azide with excess of standard silver nitrate. A little sodium acetate is added to decrease the solubility of the silver azide. The excess of silver nitrate is titrated with thiocyanate. The hydrazoic acid may also be distilled off after addition of acetic acid or ammonium nitrate and estimated as silver azide.[2]

Gasometric methods are also sometimes used.[3]

Azides and hydrazoic acid may be detected qualitatively by the red colour which they give with ferric salts.

Among other substances suggested as initiators are tetrazole derivatives, cyanuric triazide,[4] lead trinitroresorcinate, hexamethylene triperoxidediamine and others. Normal lead dinitrosalicylate has a sensitiveness to shock substantially equal to that of mercury fulminate.[5]

(c) Detonator and Cap Compositions[6]

(i) Detonator Compositions.—If the composition is contained in a metal capsule, great care is necessary in the removal of the contents, as the materials are very sensitive. It is advisable to carry out the operation by mechanical means from behind a steel screen. In some cases the detonator is cut open, in others it is squeezed with pliers under precautions to loosen the contents which are then tipped out. The composition may also be loosened by rolling the detonator carefully between two pieces of smooth hardwood board. In opening electric detonators, Taylor and Rinkenbach recommend cutting into the sulphur filling and asphalt and then peeling the copper down in a spiral until the plugs are loosened enough to be withdrawn easily.

[1] *Reichsanstalt, Ann. Rept.* V., 1926, 143.

[2] Marqueyrol and Loriette, *Bull. Soc. Chim.*, 1918 (4), **23**, 401.

[3] Sommer and Pincas, *Ber.*, 1915, **48**, 1963; Metz, *Reichsanstalt Ann. Rept.* V., 1926, 142.

[4] U.S.P. 1890378.

[5] U.S.P. 2021410 (1936).

[6] Taylor and Rinkenbach, *U.S. Bur. Mines, Bull.* **219**; Utescher, *Z. ges. Schiess- u. Sprengstoffw.*, 1911, **6**, 402; Nicolardot, *Bull. Soc. Chim.*, 1918, **4**, 163; *Ann. Chim. analyt.*, 1918, **23**, 192, 206; Langhans, *Z. ges. Schiess- u. Sprengstoffw.*, 1921, **16**, 49, 57; Marqueyrol and Loriette, *Ann. Chim. analyt.*, 1919, (2), **1**, 114; *Mém. Poudres*, 1921, **18**, 93.

The portion of the shell containing the charge should on no account be cut into.

It is of importance to observe whether the contents of a detonator consist of one layer of composition or whether they have also a separate layer of a nitro-compound. In the latter case the two layers should be separated mechanically as completely as possible. The approximate weight of the filling should be determined.

The moisture content is not usually determined; it is generally very low. The efficiency is, however, strongly affected by moisture, and the estimation may be made, if required, by drying for three days over sulphuric acid in a vacuum desiccator. A small beaker of mercury should be inserted to prevent evaporation of metallic mercury from fulminate.

The analysis of simple fulminate-chlorate mixtures may be effected by extraction either with water or with pyridine. In the former method the mixture is digested with cold water, and the residue is washed on a filter. The mercury fulminate is dried at 50° for three hours and weighed. Some fulminate dissolves in the water. This is estimated by precipitation as sulphide. The chlorate may also be determined in the filtrate. The solution is boiled with nitric acid and then treated with formaldehyde and silver nitrate. Silver chloride is precipitated and the estimation may be made gravimetrically or by Volhard's method.

Mercury fulminate is soluble in pyridine and may be extracted, leaving the chlorate undissolved. The latter is washed with ether, dried and weighed. Small quantities of impurities in the fulminate remain undissolved; these may be separated from the chlorate by extraction with water. The fulminate may be separated as sulphide after diluting the pyridine solution with water.

Binding material may be present in small quantities and is estimated by difference.

In the analysis of composite detonators containing fulminate-chlorate with tetryl or trinitrotoluene the two layers are separated mechanically; the fulminate-chlorate is dealt with as above, and the nitro-compound is examined for melting point, acidity and possibly nitrogen content. If it is not found possible to separate the two layers satisfactorily, composite tetryl detonators may be dealt with as follows: The contents of two or three detonators are extracted with water, which dissolves the chlorate and a little fulminate. These are estimated in the aqueous solution as above. The filter and its contents are dried for five hours at 70° and weighed. The fulminate is dissolved out with warm 30 per cent. hydrochloric acid, followed by five washes with water. The residue is dried for three hours at 110° and weighed. If it is required to estimate insoluble impurities, the tetryl may be dissolved in acetone or benzene.

In the examination of composite detonators containing lead azide in conjunction with trinitrotoluene or tetryl, the primary and secondary fillings are separated mechanically and tested. If it is not found possible to separate the two layers they are mixed together and the nitro-compound is extracted with absolute ether, orthonitrotoluene or other suitable solvent. The insoluble lead azide is dried at 70° and weighed. If lead trinitroresorcinate is also present, the content of lead and of azide-nitrogen is determined.

Methods are given by Taylor and Rinkenbach (*loc. cit.*) for the analysis of compositions containing fulminate, chlorate, nitromannite, and nitrocellulose.

(ii) Cap Compositions.—Percussion caps are required for ignitory purposes in fire-arms and thus differ from detonators. Antimony sulphide is frequently added for this purpose. Ignitory compositions are much more varied in nature than detonator compositions and are often complex in character. Mercury fulminate is frequently used as a constituent, but some are free from fulminate.

The compositions are very sensitive, but the charge is much smaller than in detonators, and consequently they can be handled without serious risk. It is usually necessary to extract the charges of several caps to obtain enough material for the tests. The hands should be protected by heavy gloves or cloth. Safe methods for the removal of the composition are given by Taylor and Rinkenbach.[1]

The compositions vary so much that a general scheme for the identification of ingredients cannot be given. Some indications of methods are given by Taylor and Rinkenbach and by Kast and Metz.[2]

The weight of charge is determined by emptying a sufficient number of caps and weighing them before and after emptying. If tinfoil is present, the small discs are carefully cleaned and weighed with the empty caps. Moisture is not usually determined; if necessary it may be estimated by drying in a vacuum over sulphuric acid.

A simple cap composition containing mercury fulminate, antimony sulphide, potassium chlorate and glass powder may be analysed by successive extractions with warm pyridine to dissolve fulminate and shellac, water to dissolve potassium chlorate, hydrochloric acid or aqua regia to dissolve antimony sulphide. Glass powder remains undissolved. The mercury, antimony and chlorate may be determined in the extracts.

The following method is given by Taylor and Rinkenbach for single primers.[3] The fulminate is estimated by the thiosulphate

[1] *Loc. cit.*

[2] *Chem. Unters. d. Spreng- und Zündstoffe.*

[3] *Cf.* Brownsdon, *J. Soc. Chem. Ind.*, 1905, **24**, 381.

method (see under Mercury Fulminate, p. 547). After the titration the supernatant liquor is decanted through a filter, and the antimony sulphide washed five times with hot water by decantation. The filter is dried and the sulphide on it is dissolved with hot hydrochloric acid, the filtrate being collected in the dish containing the bulk of the antimony sulphide. This is heated to expel hydrogen sulphide. About 1 g. of tartaric acid is added and the solution is transferred to an Erlenmeyer flask. Ammonia is added until the solution is nearly neutralized, but no excess should be added. The neutralization is completed with solid sodium bicarbonate and an excess of 0·05 g. is added. The solution is then titrated with $N/100$ iodine solution and starch.

If ground glass is present, it remains as an insoluble residue which may be determined. The potassium chlorate is determined by difference. Heaven [1] precipitates the mercury from the thiosulphate solution as sulphide, reduces the chlorate with ferrous sulphate and titrates the chloride formed.

Taylor and Rinkenbach give a method for such compositions, in which a sample is heated with dilute sulphuric acid and the sulphides of mercury and antimony are precipitated with hydrogen sulphide. The filtrate is evaporated, the chlorate being decomposed. The evaporation is completed in a platinum dish, and the residue is finally ignited. The potassium sulphate is weighed. The sulphides are dissolved in hydrochloric and nitric acid with addition of tartaric acid. Glass powder remains undissolved and is filtered off. The sulphides are again precipitated and separated by ammonium sulphide. The mercury is determined as sulphide, and the antimony solution is oxidized with nitric acid.

Methods are given by Taylor and Rinkenbach for mixtures containing :—

(i) Chlorate, antimony sulphide, lead sulphocyanide and trinitrotoluene.

(ii) Red phosphorus, lead picrate, and barium nitrate.

(iii) Chlorate, antimony sulphide, lead nitrate and trinitrotoluene.

(iv) Chlorate, antimony sulphide, lead nitrate, glass and trinitrotoluene.

(v) Fulminate, lead picrate, antimony sulphide, barium nitrate and barium carbonate.

(vi) Silver permanganate, antimony sulphide, trinitrotoluene and red phosphorus.

[1] *J. Soc. Chem. Ind.*, 1918, 37, 143 T.

VII. Physical and Explosive Tests[1]

The chemical analysis of explosives is frequently supplemented by physical tests. These may be combined with storage trials at ordinary temperature or under warm conditions to find whether alterations have taken place with regard to hardening, conglomeration, exudation, absorption of moisture, efficiency or stability.

Density. The method for gun-powder and similar powders is given on p. 518. The density of blasting explosives in cartridge form may be estimated by weighing and measuring the cartridges. Another approximate method is to measure the displacement of sand. A glass tube is filled with sand and weighed. It is then emptied and a weighed stick of the explosive is inserted. Sand is poured in until the tube is full. The sand is levelled off and the whole is weighed. The apparent density of the sand is determined separately in the same tube.

Tendency to Segregate. Mixed explosives may tend to separate to some extent into their ingredients by shaking or by alternations of moisture in the atmosphere. The effect of shaking may be determined by putting a quantity of the explosive into a wide-mouthed bottle, so that the bottle is partially filled. The bottle is corked and shaken in a mechanical shaker for an hour. The explosive is then examined for visible signs of segregation and separate portions may be taken out and examined for differences in ease of ignition, etc. The effect of moisture is ascertained by exposing a sample in a flat dish for alternate periods of twenty-four hours to moist and dry air and examining after a week for efflorescence of crystals.

Movement of nitroglycerine in a cartridge by gravitation is tested by keeping the cartridge in a vertical position for some weeks at 32°. Portions from the two ends are examined for nitroglycerine content before and after the test, which may be carried out in dry or moist air.

Exudation. This refers mainly to nitroglycerine explosives. Exudation is undesirable, as the liquid nitroglycerine which exudes out may become exploded by friction or shock. The exudation can be measured by placing a cylinder of the explosive on porous paper in a warm oven and ascertaining the amount of liquid which sweats out. A typical explosive is taken as a control. In a test prescribed by the Home Office, a cylinder is cut from the cartridge, such that the length is about equal to the diameter. The ends are cut flat and the cylinder is placed on a flat surface and secured by a pin. It is then kept at 85° to 90° F. for six days and nights. The cylinder must not decrease by more than a quarter of its height, and the upper surface

[1] *Cf.* Bichel, *Testing Explosives*; Marshall, *Explosives*; Lehalleur, *Poudres Explosifs et Artifices*; Findlay and Rosebourne, *J. Soc. Chem. Ind.*, 1922, 41, 58 T.; and Reilly and Rae, *Physico-Chemical Methods*, 1940.

must retain its flatness and the sharpness of its edges. Sometimes pressure is applied to facilitate the exudation, and centrifuging has also been applied. To test the exudation due to freezing, the cartridges are frozen and thawed three times. Exudation is also met with in nitro-compounds which form eutectic mixtures.

Inflammability. A small sample of the explosive is filled into a glass or paper tube about 2 cm. in diameter. The exposed surface is smoothed, and a slow fuse is brought in contact with it and ignited, to ascertain whether the explosive inflames and whether it burns partially or completely. The test should be repeated on several samples. The ease of inflammation may also be measured by playing a small bunsen flame on to the explosive for a measured time, say ten seconds. Considerable differences are observed between different explosives. Control samples of known explosives should be included for comparison. Another method is to fasten a small quantity of the explosive to the end of a pendulum which swings through a flame in such a way that the time can be measured.

If the explosive has withstood the test in which it is exposed to the flame from a slow fuse, it is further tested by dropping a portion of 0·5 g. into a red-hot iron basin 12 cm. in diameter. The quantity may be increased to 5 g. if no explosion occurs. The basin must be well cleaned after each test and should be frequently renewed ; on the other hand a new basin does not give quite normal results, until it has been used once or twice.

In some cases, larger quantities of a pound or two are burnt in a wood fire to ascertain the degree of danger to which the explosive may give rise in case of fire. The observations should be made under precautions at a safe distance.

Ignition Temperature. This is usually determined by placing 0·1 g. of the explosive in a small test-tube, which is then corked and placed in a fusible metal bath at 100°. The temperature is raised 5° per minute until inflammation or explosion occurs. The quantity and rate of heating differ in different countries. The explosibility of ammonium nitrate has been studied by Gawthorpe.[1]

Sensitiveness to Shock and Friction. The sensitiveness to blows is measured by the falling weight test. The explosive must be finely divided and well dried. A small portion is spread in a thin layer on an anvil. A bolt rests on the explosive and a cylindrical weight is allowed to fall upon it from a measured height. If explosion occurs the test is repeated with a lower height of fall until the mean height is found at which explosion just occurs. A standard explosive which can be obtained in pure condition, such as picric acid, is taken as a control. Considerable difficulty has been met with in obtaining

[1] *Army Ord.*, **6**, 47.

reproducible results. An improved method was introduced by Rotter [1] in which the results of each impact are evaluated, not by personal judgment but by a quantitative measurement of the gas produced by the decomposition of the explosive. A number of typical results are quoted by Robertson. The sensitiveness to friction may be tested qualitatively by rubbing a small portion of the explosive vigorously in an unglazed mortar with an unglazed pestle. A useful test is to strike a glancing blow with a mallet, the explosive being laid on anvils of different materials. A broomstick may also be used, the explosive being struck with the end by a blow in which the broomstick is moved in the direction of its axis at an angle of about 60° to the anvil. A more scientific test on these lines is described by Howell.[2] His apparatus consists of a steel anvil with grooves to hold the

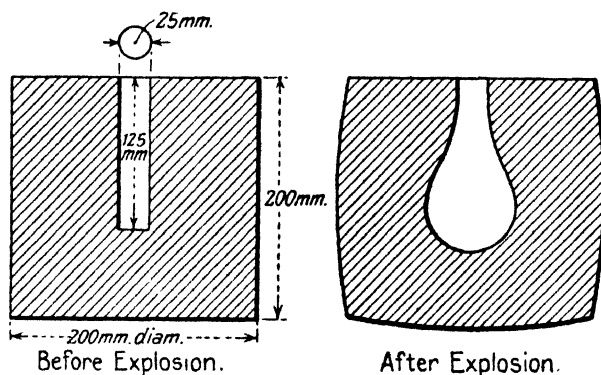



FIG. 121.

explosive (7 g.), and a swinging shoe which is allowed to fall with a circular motion from various heights.

Lead Block Test. This is one of the oldest tests for the explosive power, and is still widely used. The explosive is fired in a cavity in a cylindrical lead block. The cavity becomes enlarged and the increase of volume is taken as a measure of the power. Standard conditions were laid down at the Fifth International Congress of Applied Chemistry. The lead block (Fig. 121) is cylindrical and is 200 mm. in height and 200 mm. in diameter. The cylindrical cavity is 125 mm. deep and 25 mm. in diameter. 10 g. of explosive wrapped in tinfoil is taken for the test, and tamped with sand. The charge is fired by a detonator, and the expansion is measured by finding the volume of water necessary to fill the cavity. The original capacity of the bore is deducted and allowance should be made for the expansion due to the detonator. The purity of the lead and the temperature

[1] *Cf.* Robertson, *J. Chem. Soc.*, 1920, **117**, 16.
[2] *U.S. Bur. Mines, Tech. Paper* 234.

of casting of the blocks affect the results to some extent. The significance of the test is dealt with by Naoum.[1]

Ballistic Pendulum. A heavy mortar is suspended from a bearing and a stemmed shot is fired into it from a steel gun. The degree to which the pendulum swings gives a measure of the energy imparted to it. The weight of the mortar and height of suspension differ in different countries, *e.g.* at Rotherham 5·025 tons at 92 in., in America 14·1 tons at 89·75 in. The gun is brought to a measured distance from the mortar and fired electrically. Charges of $\frac{1}{4}$ to $\frac{1}{2}$ lb. of explosive are used, and a standard explosive is taken for comparison.

In another method a heavy mortar, firing at an elevation of 30°, is used. The explosive is detonated by means of a slow fuse and propels a projectile weighing 15 kg. The distance to which this is thrown is measured.

Brisance Meter. In using this apparatus, the violence of the explosive effect is measured by the crushing of a metal cylinder. The explosive is detonated on a steel plate, covered by two lead discs for protection. The steel plate is 2 cm. thick, weighs 320 g. and is supported by a piston fitting into a hollow steel cylinder. The lower end of the piston rests on a copper cylinder supported by the steel base. The detonation of the explosive transmits a pressure through the piston to the copper cylinder, and crushes it to an extent which can be measured. The degree of crushing is used to compare the brisance of different explosives.

Rate of Detonation. Two methods are in use. In the direct method, the time of detonation of a measured length of a column of explosive is determined. This necessitates the accurate measurement of very short time intervals, which is effected by means of a rapidly rotating drum fitted with a speed recorder. The column of explosive is fitted with wires at a fixed distance apart, generally one metre. The rupture of the wires gives rise to induction sparks, which give spots on the smoked surface of the drum. By measuring the distance between the spots, the rate of detonation can be calculated. The velocity depends upon the diameter of the train of explosive up to a limiting value, the degree of confinement, the density, and the method of initiation.

An alternative method is that of Dautriche. This method is a comparative one and necessitates a knowledge of the rate of detonation of a standard explosive enclosed in a detonating fuse. The explosive to be tested may be in cartridges or compressed into a tube; a detonator is inserted at one end (Fig. 122). Two other detonators are inserted into the sides of the tube at a known distance apart, and connected to a loop of the detonating fuse. When the explosive is

[1] *Z. ges. Schiess- u. Sprengstoffw.*, 1932, **27**, 181, 229, 267.

detonated the detonation is transmitted successively to the two ends of the detonating fuse, and the two waves meet at a point depending on the rates of detonation of the main explosive and of the explosive in the detonating fuse. The point at which the waves meet is ascertained by the indentation of a slab of lead on which the detonating fuse lies.

The sensitiveness to detonation is determined by subjecting the explosive in its usual form (*e.g.* in cartridges) to the action of detonators of different intensities. These are fired electrically, and the effect on the explosive is observed.

In order to ascertain the propagation of detonation, two cartridges are placed end to end on the ground at a certain distance apart, and one of them is detonated. By varying the distance it can be ascertained at what distance the first cartridge is able to detonate the second.

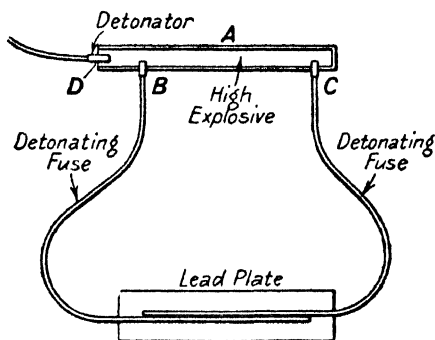



FIG. 122.

Length and Duration of Flame. These are of importance in connection with the ignition of fire-damp, etc. The measurements are made photographically. A sensitive film is fixed to a drum, which is rotated at a known speed, and the flame is photographed through a narrow slit in such a way that the height of the image shows the length of the flame and the breadth shows its duration.

Testing of Detonators. A review of the methods used for detonators is given by Kast and Haid.[1] The initiating action may be determined by the Esop and Wöhler tests in which the detonator is fired in contact with an explosive which has been partially deadened by the addition of an inert substance. Tests are also made to determine the limiting charge of a detonator composition, which just suffices to bring about detonation. In the "Sand test" of the U.S.A. Bureau of Mines, a detonating charge is exploded in a mass of carefully graded sand and the degree of pulverization caused by the explosion is measured.

[1] *Z. ges. Schiess- u. Sprengstoffw.*, 1924, 19, 146.

In the " Nail test " the detonator is attached by means of wire to a nail, the two being parallel and the lower end of the detonator being level with the centre of the nail. The power of the detonator is measured by the degree of bending of the nail. Standard nails must be used for the test.

The Trauzl test is sometimes used with a smaller lead block. The indentation of a lead plate is also frequently made use of. Methods for caps are given by Brownsdon.[1] These include photographs of the flash with the help of a revolving perforated disc, to determine the length and duration of flash, measurements of the heat evolved and the volume of gas generated, in a special apparatus.

The effect of light on trotyl has been studied by Kraus and Turek.[2]

C. STABILITY TESTS

Nitric esters undergo gradual decomposition on storage. Stability tests are therefore necessary as a control of the safety of explosives of this type. The tests are applied during manufacture and to the finished explosive ; and they may also be applied at intervals during storage, especially in hot climates.

The usual procedure in stability tests is to subject a sample of the explosive to a raised temperature in order to increase the rapidity of the decomposition and obtain a quick indication of the stability. After heating at constant temperature for a certain length of time, the degree of decomposition is measured by one of the following methods :—

(1) By indicators depending on the action of nitric peroxide.
(2) Direct observation of brown fumes.
(3) Measurements of spontaneous heating.
(4) Methods depending on the explosion of the sample.
(5) Quantitative estimations of decomposition products.
(6) Loss of weight.
(7) Gasometric methods.
(8) Acidity measurements.

The most reliable procedure is to carry out a heating trial at a temperature not far removed from the temperature of storage, but this necessitates a prolonged trial in order to bring about a measurable degree of decomposition, and is not always practicable.

[1] *J. Soc. Chem. Ind.*, 1905, **24**, 381 ; *cf.* also Borland, *ibid.*, 1906, **25**, 241.
[2] *Z. Schiess- u. Sprengstoffw.*, 1925, **20**, 49.

I. Stability Tests depending upon Indicators for Nitric Peroxide

(a) Abel Heat Test

This is the oldest test, but is still widely used. It depends upon the colorimetric estimation of traces of nitrous acid or nitric peroxide by test papers prepared with potassium iodide and starch. The explosive is contained in a test-tube which is heated to a constant temperature, the test paper being suspended over the explosive.

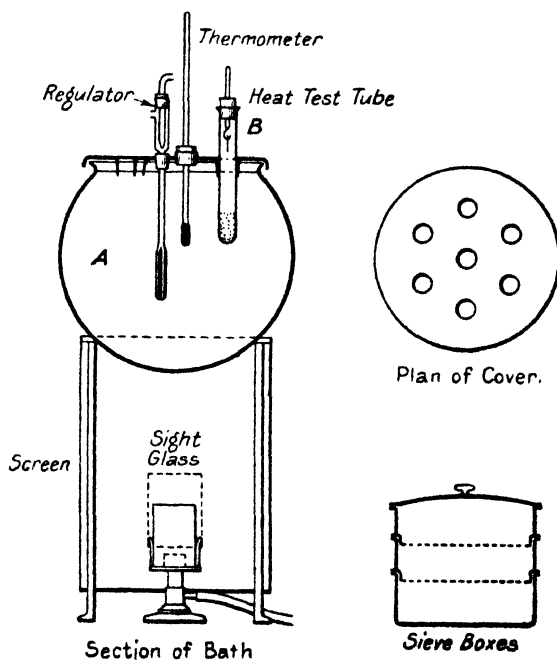



Fig. 123.

Precise details for the test are laid down in a Report on the Heat Test as applied to Explosives.[1] The following are the main requirements. Apparatus of the standard patterns can be obtained from chemical apparatus dealers.

Heating Bath (Fig. 123). The bath consists of a spherical copper vessel 7⅝ in. diameter with an aperture of 5⅝ in. It has an overflow pipe ⅜ in. below the top. The lid is of copper about 6 in. in diameter and has 7 holes, one for a thermometer and six for the glass tubes. These are held in position by wire supports fixed to the lower side of the lid. The bath rests on a tripod stand surrounded by a screen, and is heated by an Argand burner with a copper chimney.

Test Tubes. These are of glass, without lips, and are 5⅜ to 5½ in. in height. They are of such diameter that they will hold 20 to 22 ml. of water when filled to

[1] H.M. Stationery Office.

a height of 5 in. They are etched with short lines at 3, 3⅜ and 5 in. from the bottom. Rubber rings are provided which fit round the test-tubes and rest on the bath lid.

Rubber Stoppers. These fit the test-tubes; they are perforated and carry a glass rod, terminating at its lower end in a platinum hook to hold the test paper.

Dropping Bottle. This is for moistening the test papers with glycerine water. It is of brown glass and has a glass stopper which is drawn out to a thin-pointed rod, which dips into the liquid.

Lead Discs. To cover any holes in the lid which are not occupied.

Caps for Test Tubes. These are of black paper; they are of cylindrical shape and fit loosely over the tubes to exclude light. They have holes near the top and bottom to permit of convection of air.

Cordite Mill. This is of the coffee-mill type with a fluted grinding surface.

Cordite Cutter. A standard pattern of knife of the lever type is prescribed for cutting up cordite, etc.

Sieves. A circular brass or copper nest of sieves of standard dimensions is used. Ground cordite is collected between two sieves, consisting of sheets of brass drilled with holes 0·08 and 0·032 in. in diameter respectively. The lower sieve fits into a circular box, and the upper sieve has a domed lid.

Rectangular Sieve (for nitrocellulose). A brass frame of internal dimensions 7⅞ in. by 5½ in. is covered with tinned brass wire gauze with 10 meshes per inch.

Test Papers. These are prepared by dipping filter paper in a solution of starch and potassium iodide. The sensitiveness depends so much upon the paper used and the conditions of preparation that it is advisable to obtain them from a standard source.

The test papers are prepared as follows: 220 ml. of freshly distilled water is placed in a flask of Jena glass and raised to boiling over a spirit lamp burning pure spirit. 3 g. of pure starch (cornflour) previously purified by washing six times by decantation with pure water and carefully dried, is suspended in 30 ml. of pure water and poured into the 220 ml. of boiling water with continuous shaking. The whole is boiled gently, with shaking, for five minutes. The starch solution is then added to a solution of 1 g. of pure potassium iodide in 250 ml. of freshly distilled water. After standing overnight in a dark room, the clear supernatant liquid is carefully syphoned off and used at once for dipping the paper. The filter paper should be of pure cotton cellulose, free from size or loading and from all trace of impurity. The prescribed thickness is 0·18 mm. Sheets of the paper are passed singly through the iodide starch solution, which is contained in a porcelain tray. Each sheet is then held vertically over the tray, and excess solution is removed from the edges by a glass rod. The sheets are then hung up to dry in the dark. They are afterwards cut into strips 1 cm. by 2 cm., the edges of the paper being discarded. Freedom from laboratory fumes is essential in all these operations. The papers are allowed to mature for a month or more in the dark before use. They are preserved in brown glass bottles. To confirm that test papers are still serviceable after keeping, a drop of dilute acetic acid is placed on the paper; this should give no coloration for some time.

Standard Tint Papers. 0·48 g. of the finest yellow ochre, 0·2 g. of raw umber and 5 g. of fine gum arabic all finely ground are shaken with 100 ml. of cold water until the gum has dissolved. The suspension is then well shaken and allowed to stand for an hour. Lines are ruled on filter paper with this suspension which is then cut up into strips 1 cm. by 2 cm. The breadth of the line must be between 0·5 and 1 mm.

Preparation of Samples for Test. Great cleanliness of the hands and all apparatus should be observed. Undue exposure of the

explosives to light should be avoided in all the operations, and the test should be carried out without delay when the sample is prepared.

A. *Explosives of Class 3, Nitro-compound, Division I*

1. *Dynamite and other Nitroglycerine Preparations from which the Nitroglycerine can be extracted by Water as below.* A glass funnel (5·5 cm.) is fitted with a filter paper. The explosive is loosened from its cartridge; 13 g. is placed in the funnel and pressed down fairly tightly with a flat-ended glass rod. The funnel is placed in a heat-test tube and filled up with distilled water. The stem of the tube must not touch the side of the heat-test tube. The water displaces nitroglycerine from the dynamite, and when 2 ml. of nitroglycerine have collected in the tube the extraction funnel is removed. No water must pass into the heat-test tube. The sample is then ready for heat test.

2. *Carbonite, Monobel Powder, and similar Friable Nitroglycerine Preparations from which the Nitroglycerine cannot conveniently be extracted as above.* The contents of the cartridge are loosened, and 3·2 g. weighed into a scoop and transferred by means of an aluminium funnel to a heat-test tube, collected at the bottom by tapping gently and pressed down to a height of 3 cm. with a flat-ended glass rod.

3. *Blasting Gelatine, Gelatine Dynamite, Gelignite, and Analogous Preparations.* The wrapper is opened, about half an inch of the end of the cartridge is cut off and discarded, and a portion weighing approximately 3·2 g. then cut off, avoiding contact with the hands. The portion is placed on the scoop and the weight is adjusted to 3·2 g. This is then transferred to a mortar and 6·5 g. of French chalk added. The explosive and French chalk are worked together with the pestle. This should require a half to one and a half minutes. The mixture is then ground by a circular movement of the pestle for half a minute, and should then be homogeneous in appearance. The mixture is transferred to a heat-test tube with the help of a horn spatula and aluminium funnel, and gently pressed down with a flat-ended glass rod to a height of 5 cm.

4. *Cordite, Ballistite and other Propellants of Class 3, Nitro-compound, Division I.* (*a*) Explosives in the form of sticks or tubes. The sticks or tubes are wiped with clean filter-paper and are cut into small pieces about ⅛ in. long with the cordite knife, ½ in. being rejected from each end of the stick or tube. The set of sieves is placed under the mill, and the cut sample is ground. The first portion is rejected and a sufficient quantity of the sample is to be taken to ensure that the portion collected between the two sieves will suffice for the test. The nest of sieves is closed and shaken for one minute. The material

collected on the second sieve is taken for the test, except that when the nominal diameter of the sticks or tubes is less than 0·03 in. the material from the bottom compartment is to be taken for the test. 1·6 g. is weighed out in the scoop, transferred by means of an aluminium funnel to a heat-test tube and shaken down by tapping the tube with the fingers.

(*b*) Explosives in the form of grains for small arms: 1·6 g. is weighed into the scoop and transferred by an aluminium funnel to the heat-test tube. Three such samples are weighed out.

B. *Explosives of Class* 3, *Nitro-compound, Division* 2

1. *Nitrocellulose Pulp.* Six thicknesses of filter paper are laid on top of one another. Sufficient of the sample to give about 5 to 6 g. after the final pressing is spread on the top sheet. Six other thicknesses of filter paper are similarly laid over the sample. The whole is then placed under pressure (*e.g.* in a hand-screw press) for about three minutes. The sample is then removed, rubbed up by hand on the filter paper and again pressed for three minutes on fresh filter paper. It is then transferred to the rectangular 10-mesh sieve and rubbed through it with the hand. 5 g. is weighed out and spread evenly on an aluminium tray. The tray is placed in the oven, which should be at 120° F. (48·9° C.), and is kept there for fifteen minutes with the door closed. It is then removed and the sample is transferred to the top sieve of the nest of sieves. It is sieved, with the lid on, for two minutes. For this operation the second sieve is not used. The portion which passes through is again spread on an aluminium tray and exposed to the air of the room for four hours. 1·3 g. is then weighed into the tube with the aid of the scoop and aluminium funnel. Two such quantities are taken. The material in each tube is pressed down with a flat-ended glass rod to a height of 3 cm.

2. *Compressed Gun-cotton for Torpedo Warheads and Mines.* About 10 g. is removed from the centre of the primer or slab by scraping with a horn spatula. The scrapings are placed in a glass beaker of 1500 ml. capacity, two-thirds full of distilled water, and stirred frequently for fifteen minutes. After settling, the water is poured off and replaced by the same quantity of water. It is again stirred for fifteen minutes, allowed to settle and decanted. The sample is collected by hand and the excess of water squeezed out. The wet gun-cotton is spread on six thicknesses of filter paper. Six other filter papers are laid on top and the sample is treated as described above for nitrocellulose pulp.

3. *Tonite and Analogous Nitrocellulose Preparations.* The sample is held over the rectangular sieve, and sufficient for the tests is scraped

out from the centre of the cartridge with a horn spatula. The material is rubbed through the sieve by hand, and spread evenly on an aluminium tray. This is placed in the oven at 120° F. (48·9° C.) for fifteen minutes with the door closed. It is then removed and the sample transferred to the top sieve of the nest of sieves. It is sieved for two minutes with the lid on. For this operation the second sieve is not to be used. The sieved material is again spread on an aluminium tray, and exposed to the air of the room for four hours. 1·3 g. is weighed out on a scoop and transferred by an aluminium funnel to a heat-test tube. Two such quantities are spread out. The material is gently pressed down with a flat-ended glass rod to a height of 3 cm.

4. *Nitrocellulose Propellants.* (*a*) Explosives in the form of sticks or tubes: the procedure as for cordite in sticks or tubes is followed. (*b*) Explosive in the form of grains for small arms. A quantity sufficient for the tests is spread evenly on an aluminium tray. This is placed in the oven at 120° F. (48·9° C.) for fifteen minutes with the door closed. It is then removed and exposed to the air of the room for four hours. Three quantities of 1·3 g. each are weighed out with a scoop, transferred by an aluminium funnel to heat-test tubes, and shaken down by tapping the tubes with the fingers.

5. *Ammonite, Bellite, Roburite, etc.* The contents of the cartridge are loosened. The first half inch is rejected, and 1·3 g. loosened into the scoop and transferred by means of an aluminium funnel to a heat-test tube.

C. *Explosives of Class* 4, *Chlorate Mixtures, Divisions* 1 *and* 2

These are treated as under Class 3 (p. 562).

Application of the Test. The heating bath is filled with water up to the outflow. It is placed in a north light in such a position that the papers can be observed by reflected light. The temperatures for the test with various explosives are given below.

The glass rod with platinum hook is inserted in the rubber stopper. A test paper is then held with forceps and pierced near the top with a needle. A small quantity of a mixture of equal volumes of glycerine and water is applied to the upper edge of the paper by means of the glass rod of the dropping bottle, so that it will moisten the upper half of the paper by the time the test is complete. The wetting of the paper requires considerable practice to ensure uniformity. The paper is then affixed to the platinum hook. At no time should the paper be touched with the fingers. The rubber stopper carrying the test-paper is inserted in the test-tube containing the explosive, so that the bottom of the stopper coincides with the top line etched on the tube, and the position of the glass rod is adjusted so that the lower

edge of the wet portion of the test paper coincides with the middle etched line on the test-tube. The lower edge of the wet portion should be approximately horizontal. The test-tube is then inserted in one of the holes of the bath so that the bottom line etched on the tube coincides with the lid of the bath. The tube should be fitted with a rubber ring flush with the lid of the bath. The cap is placed over the tube. The cap is lifted at intervals to observe the test paper, but should not be lifted unnecessarily. The test is completed when the faint brown line which appears on the paper becomes equal in depth of tint to the standard tint. The time is measured from the introduction of the tube into the bath, to the production of a tint equal to the standard tint. The following table summarises the limits for the different explosives :—

Abel Heat Test: Quantities, Temperatures and Time Limits

	Temperature.		Quantity.	Time Limit.
	Degree F.	Degree C.		Minutes.
Class 3, *Division* 1.				
Nitroglycerine extracted from dynamite, etc.	160	71·1	2 c.c.	15
Carbonite, Monobel and similar explosives from which the nitroglycerine cannot conveniently be extracted by water	160	71·1	3·2 g.	7
Blasting gelatine, gelatine dynamite and analogous preparations	160	71·1	3·2 g. +6·5 g. French chalk	10
Cordite,* ballistite and other propellants of Class 3, Division 1	160	71·1	3·2 g.	10
Class 3, *Division* 2.				
Nitrocellulose pulp, compressed guncotton, tonite and analogous compressed nitrocellulose preparations	170	76·7	1·3 g.	10
Nitrocellulose propellants . . .	170	76·7	1·3 g.	10
Ammonite, bellite, roburite, and analogous preparations	170	76·7	1·3 g.	10

* For the acceptance of New Cordite and Cordite MD for the British Naval and Military Services the details are as follows :—

Cordite and Cordite MD	180	82·2	1·6 g.	30

Mechanism of the Abel Heat Test. The test depends upon the liberation of iodine from the potassium iodide by nitric peroxide. The quantity of nitric peroxide necessary to colour the paper to the standard tint is very small. Robertson and Smart[1] found it to be 0·000135 mg.

[1] *J. Soc. Chem. Ind.*, 1910, **29**, 130.

The relation between the time of the test and the concentration of nitric peroxide was also studied by Robertson and Smart. A lag of about four minutes occurs at the start, due to the time of heating of the explosive. In some cases, however, the action on the test paper is not due wholly to decomposition during the test, but is in part due to nitric peroxide dissolved in the explosive.[1]

The test has been frequently criticised on account of the minute quantity of nitric peroxide which is measured. This necessitates exact adherence to standard conditions of working in regard to the design of apparatus, preparation of the test-papers, etc. The exact end-point is somewhat difficult to determine, and is liable to be affected by the illumination, notwithstanding the use of a standard tint for comparison.

In some cases the traces of decomposition measured may be due to relatively harmless impurities. The test may also be shortened by traces of oxidizing substances, such as organic peroxides which liberate iodine from potassium iodide ; on the other hand, the test may be masked by certain substances such as mercury.[2]

The quantity of moisture present (in gun-cotton, for instance) may affect the results ; if moisture condenses on the sides of the tube, nitric peroxide is absorbed. If, on the other hand, the test paper becomes too dry, the sensitiveness is decreased.

According to Köhler and Marqueyrol[3] calcium carbonate does not affect the test directly, but in presence of water it gives rise to hydrolysis of nitrocellulose and forms traces of calcium nitrite, which lower the test.

For the above reasons the test has been given up in Germany.[4] If, however, the conditions be closely adhered to, it serves a useful purpose, especially in the manufacture of nitric esters. It is also very simple to apply, and is used to a considerable extent in this country and in France.

Attempts were made at an early date to overcome the masking of the test by the use of other indicators in place of potassium iodide and starch. The zinc iodide test is, of course, open to the same criticisms.

(b) Zinc Iodide Test

This is a German modification of the heat test. Zinc iodide is used in place of potassium iodide. This renders the test rather more sensitive. The conditions of testing are given by Kast and Metz.[5]

[1] See also Smart, *J. Soc. Chem. Ind.*, 1913, **32**, 967 ; Egerton, *J. Soc. Chem. Ind.*, 1913, **32**, 331 ; 1914, **33**, 112.

[2] Guttmann, *J. Soc. Chem. Ind.*, 1897, **16**, 283.

[3] *Mém. Poudres*, 1928, **23**, 11.

[4] *Reichsanstalt, Ann. Rept.*, 1922-3, I., 41 ; 1927, VI., 129 ; *cf.* Lenze and Metz, *Z. ges. Schiess- u. Sprengstoffw.*, 1928, **23**, 340, 381, 428 ; Metz, *ibid.*, 1932, **27**, 118, 150.

[5] *Chem. Unters. d. Spreng- u. Zündstoffe*, p. 227.

(c) Guttmann's Test [1]

Guttmann used a solution of diphenylamine in sulphuric acid as indicator to overcome the masking effect of mercuric chloride, etc., on the Abel test. Jannopoulos [2] described a modification in which the finely ground powder is previously warmed to 35-38° for four days before testing. The tests are inapplicable to nitroglycerine powders, as the nitroglycerine vapour is decomposed by the sulphuric acid.

(d) Hoitsema's Test [3]

Diphenylamine was also used in this test, but was applied on glass wool instead of paper.

(e) Spica's Test [4]

In this test a solution of metaphenylenediamine hydrochloride was used. This is unduly sensitive and the indicator has poor keeping properties.

Various other reagents, such as indol, sulphanilic acid and alpha-naphthylamine, dimethylaniline, beta-naphtholsulphonic acid, etc., have also been tried as indicators.

(f) Hess Test [5]

In this test the explosive was heated at 70° in a current of air, which was passed into a solution of zinc iodide and starch. The time taken to impart a blue colour to the solution was noted.

(g) Vieille Test [6]

In this test the decomposition is carried considerably further. 10 g. of the explosive is weighed into a glass tube, and a strip of litmus paper is placed in the upper part of the tube. The tube is corked and placed in a water-jacketed oven, the jacket being maintained at 110°. The actual temperature of the explosive is approximately 108·5°. If the litmus turns colour within ten hours, the tube is at once removed; otherwise the tube is removed after ten hours. In either case the explosive is exposed to the air overnight, and on the following day it is reheated similarly with a fresh strip of litmus. This is repeated every day until the colour-change occurs within

[1] *Z. angew. Chem.*, 1897, **10**, 233, 265; *J. Soc. Chem. Ind.*, 1897, **16**, 283.

[2] *Int. Congr. Appl. Chem.* VII., 1907, II., 605.

[3] *Z. physikal. Chem.*, 1898, **27**, 567.

[4] *Atti Reale Ist. Veneto di Scienze*, 1899, **58**, 27, 289.

[5] *Mitt. über Gegenst. d. Art. u. Geniew.*, 1879, 345.

[6] *Réglements de Réception des Nitrocelluloses et poudres dans les Poudreries françaises; cf.* Jacqué, *Z. ges. Schiess- u. Sprengstoffw.*, 1906, **1**, 205, 395; Patterson, *ibid.*, 1910, **5**, 49.

an hour. The total number of hours of heating is then taken as a measure of the stability. The following limits are given by A. P. Sy[1]: for large powders thirty hours; for small powders twenty hours; for ungelatinized nitrocellulose ten hours.

The test has been used mainly in France. A somewhat modified test has been used in Italy.[2]

(h) Horn-Seifert Test [3]

In the original test of Horn, 2 g. of powder was heated in a long test-tube at 120°, and nitric peroxide was observed by looking down the length of the tube. A disc of white porcelain was laid on the surface of the powder to facilitate the observation. Seifert modified the test by introducing a test paper (methyl-violet and rosaniline) and observing the successive changes of colour.

(i) Continuous Stability Test [4]

The case in which the explosive was stored was fitted with a narrow metal tube communicating with a glass tube containing a porous material impregnated with litmus or other indicator. The gases evolved by the explosive on storage reacted with the indicator.

(j) Methyl Violet Test [5]

Methyl violet is gradually turned blue green, and ultimately a pale salmon colour by nitric peroxide. It is much less sensitive than starch iodide. For the test, 2·5 g. of the dried sample of explosive is placed in a glass tube 29 cm. long and 1·5 cm. internal diameter. The sample is pressed down to occupy a depth of 5 cm. and a methyl violet paper is placed in the tube with its lower edge 2·5 cm. above the explosive. The tube is inserted in a bath at 134° to 135° so that about 6 to 7 mm. of the tube projects from the bath. After twenty minutes the tube is partially withdrawn to examine the paper, and this is repeated at intervals of five minutes until the paper becomes salmon-pink. The time of the test should be at least thirty minutes. The papers are prepared by dipping Schleicher and Schüll's filter paper No. 597 in a solution of pure rosaniline acetate (prepared from 0·25 g. basic rosaniline), 0·168 g. methyl violet (crystal violet), 4 ml. glycerine, 30 ml. water, made up to 100 ml. with pure 95 per cent. alcohol. The dried paper is cut into strips 2×7 cm.

[1] *J. Franklin Inst.*, 1903, **155**, 161. [2] Bravetta, *Z. ges. Schiess- u. Sprengstoffw.*, 1912, **7**, 496.

[3] Seifert, *Vojensko Technicke Zprovy*, 1927, **4**, 42.

[4] Bouchaud-Praceiq, *Z. ges. Schiess- u. Sprengstoffw.*, 1909, **4**, 96; Swiss Pat. 41445/1908.

[5] *Cf.* O'Hern, *Journ. U.S. Artill.*, 1913, **40**, 148; Lenze and Metz, *Z. ges. Schiess- u. Sprengstoffw.*, 1928, **23**, 340, 381, 428; Wiggam and Goodyear, *Ind. Eng. Chem.*, 1932, **24**, 75.

(k) Pollard's Test [1]

This depends upon the action of nitric peroxide on colloidal silver oxide. A current of air is passed over the powder and into a colloidal solution of silver oxide. The nitric peroxide reacts with the silver oxide and decreases the amount of light diffused by the colloid. The decrease forms a measure of the decomposition of the nitric esters.

(l) Jensen's Test [2]

Nitrocellulose powder is heated gradually from 100° upwards as in the deflagration test. A strip of iodide paper is suspended over the powder and the temperature at which the test paper gives a coloration is taken as an indication of the stability of the powder.

II. Stability Tests depending on the Direct Observation of Brown Fumes

(a) Simon Thomas Test (1898) [3]

The explosive is heated at 100° for eight hours each day until visible fumes appear. The test has subsequently been used in Holland in a slightly altered form.[4] A quantity (usually 2½ g.) of explosive is heated to 95°, first for four hours in an unstoppered flask, and then for eight-hourly periods. In general nitrocellulose requires fourteen to twenty-four daily periods. The test is stated to give good results for ungelatinized nitrocellulose, but to be less satisfactory for propellants.

(b) American Test at 65·5° or 80° [5]

A hard glass-stoppered bottle of 8 oz. capacity is filled to one-third with the propellant and maintained at 65·5° or 80° until brown fumes appear. The time of the test ranges up to 300-400 days at 65·5° or 75-100 days at 80°. As the powder deteriorates, the time of the test decreases until ultimately tests of one to six days are obtained.

(c) International 75° Test [6]

Two samples of 10 g. each are placed in capsules 35 mm. diameter and 50 mm. in height; the capsules are loosely covered with watch-glasses, and are heated for forty-eight hours at 75°. The appearance and odour of the powder and the formation of nitrous fumes are

[1] *Trans. Opt. Soc.*, 1924-25, **26**, 63. [2] *Tidsskrift for Søvaesen*, 1928, **99**, 407.

[3] *Z. angew. Chem.*, 1898, **11**, 1027; 1907, **20**, 1143.

[4] De Bruin, *Z. ges. Schiess- u. Sprengstoffw.*, 1922, **17**, 59; *Rec. trav. chim.*, 1921, **40**, 642.

[5] Patterson, *Z. ges. Schiess- u. Sprengstoffw.*, 1910, **5**, 47; O'Hern, *Smithsonian Rept.*, 1914, 257; Wiggam and Goodyear, *Ind. Eng. Chem.*, 1932, **24**, 72.

[6] *Int. Congr. Appl. Chem.* VIII., 1912, Appendix, Section III. (*b*), 311.

noted. If there is any positive indication of decomposition the explosive is considered to be of unsatisfactory stability.

(d) Warmlagermethode 75°[1]

This test is largely used in Germany for nitrocellulose and propellants. 5 g. of the explosive is heated in stoppered tubes of 200 mm. length and 28 mm. diameter at 75°. The tubes are left open for sixteen hours and are then stoppered, and the heating is continued without interruption until distinct brown fumes appear. They are opened once a week for ten minutes to renew the supply of oxygen necessary to convert NO to NO_2. The test is stated to give reliable results and to give good concordance in tests done on the same powder at different times. V. Meerscheidt-Hüllessem[2] has described an improved form of apparatus for the test. A temperature of 100° is sometimes used.

III. Stability Tests depending on Spontaneous Heating of the Explosive

As long ago as 1884 Hess proposed a test in which the explosive was maintained at 70° until spontaneous heating set in, but this did not come into use.[3]

(a) Silvered Vessel Test[4]

This test was devised by Robertson for the testing of cordite. The apparatus consists of a vacuum-jacketed flask, which is maintained at 80° in a bath. The cordite is ground as for the heat-test, and 50 g. is placed in the flask. A thermometer is fitted in the neck of the flask with its bulb in the ground cordite. The neck of the flask has a lateral side-tube for the observation of brown fumes of nitric peroxide. The test is continued until the thermometer shows a rise of 2° due to spontaneous heating of the cordite. The time is then noted, and taken as a measure of the stability. The test usually requires several hundred hours, but the time varies greatly with the nature of the powder. Further details and comments are given by Brunswig,[5] Tonegutti,[6] Vignau and Babuglia,[7] and Marshall.[8]

[1] Lenze and Pleus, *Z. ges. Schiess- u. Sprengstoffw.*, 1919, **14**, 317; Lenze and Metz, *ibid.*, 1928, **23**, 340, 381, 428; Stettbacher, *ibid.*, 1929, **24**, 172; *Chem. Zeit.*, 1925, **49**, 646.

[2] *Z. ges. Schiess- u. Sprengstoffw.*, 1930, **25**, 141.

[3] *Dingl. Polyt. J.*, 1884, **251**, 120.

[4] *Regulations for Army Ordnance Services*, Pt. II. (Wyman); Nathan, *J. Soc. Chem Ind.*, 1909, **28**, 443.

[5] *Das rauchlose Pulver*, p. 399.

[6] *Annali Chim. Appl.*, 1925, **15**, 548.

[7] *Brit. Chem. Abstr.*, 1926, B, 723.

[8] *Explosives*, 2nd Ed., p. 663.

(b) Taylor's Test [1]

In this test 4·5 g. of nitrocellulose is heated in a tube 30 cm. long and 1·4 cm. in diameter at 135°. A thermometer is fixed with its bulb embedded in the nitrocellulose, and the heating is continued until a rise of temperature is indicated. This usually requires forty-five to sixty minutes.

IV. Tests in which Decomposition is carried to Explosion

(a) German 132° Test [2]

This test has been used to a considerable extent in Germany for the testing of nitrocellulose and powders. The nitrocellulose is dried and heated in a glass tube. Observations are made of the change of colour of litmus paper, the formation of brown fumes and the explosion of the samples. The test was formerly carried out at 135°, but is now carried out at 132° and the observations are frequently confined to the brown fumes. For the test as formerly carried out the following limits were given by Sy.[3]

	Litmus.	Fumes.	Explosion.
Ungelatinized nitrocellulose .	30 mins.	45 mins.	5 hrs.
Nitrocellulose powder . .	75 ,,	120 ,,	5 ,,
Nitroglycerine powder . .	30 ,,	45 ,,	5 ,,

In the test as now carried out, 2·5 g. of the sample of nitrocellulose or smokeless powder is placed in a tube 350 mm. long, 16 mm. internal diameter, and 19 mm. outer diameter. A strip of blue litmus is pushed down so that it is 25 mm. above the explosive. The glass tube is loosely closed with a cork disc or a paraffined cork, and put into a bath containing boiling xylene, with a reflux condenser. The cover of the bath is provided with orifices to hold the tubes. The orifices are 11 cm. deep and contain glycerine.

Uniformity of the litmus is of great importance. Vignau and Angli [4] describe a modified apparatus to avoid loss of vapour and minimize the effects of explosion. V. Meerscheidt-Hüllessem [5] describes a bath in which the appearance of the explosive may be observed during the heating.

[1] *Ind. Eng. Chem.*, 1924, **16**, 1185.

[2] Escales, *Die Schiessbaumwolle*, 1905, p. 183; Worden, *Nitrocellulose Industry*, 1911. p. 971; Kast and Metz, *Chem. Unters. d. Spreng- u. Zündstoffe*, 1931, p. 233.

[3] *J. Amer. Chem. Soc.*, 1903, **25**, 554.

[4] *Brit. Chem. Abstr.*, 1926, B, 723.

[5] *Z. ges. Schiess- u. Sprengstoffw.*, 1929, **24**, 10.

(b) Deflagration Test [1]

A bath of mineral jelly is heated to 100°. Test-tubes, each containing 0·1 g. of explosive, are suspended in the bath, and the temperature is then raised at the rate of 5° per minute. Little paper caps are lightly fixed on the mouths of the tubes to indicate which sample has exploded. The temperatures of explosion are noted. Berl and Rueff [2] described an apparatus consisting of a copper block, heated electrically, with holes for the test-tubes.

A combination of the deflagration test with the Abel test is given by Jensen.[3]

(c) Time to Explosion

In some cases the explosive is maintained at constant temperature, and the time to explosion is measured. Patterson [4] gives a number of results, of which the following is an example :—

Temperature	136°	139·5°	143°	148°	160°	168°
Time to explosion	5 hrs.	2 hrs.	1 hr.	30 m.	16 m.	12 m.

Weber [5] describes an apparatus in which the powder is heated in glass tubes at 160°, 170°, 180° and 200° and the time to explosion is measured. Wiggam and Goodyear [6] have made a critical study of the explosion-time test.

V. Quantitative Determination of Nitric Peroxide

Bergmann and Junk Test [7]

This test is widely used for the testing of nitrocellulose. The apparatus is shown in Fig. 124. The heating tube consists of a glass tube, 35 cm. long and 19 mm. in diameter. The ground-glass neck is fitted with an absorption vessel containing water. The nitrocellulose is well dried and 2 g. is placed in the tube, which is then heated in a bath of special construction. The bath is maintained at 132° by a boiling liquid. After two hours' heating the tube is removed from the bath, and water is poured into the cup. As the tube cools, the water is drawn into the main tube. The cup is rinsed out with water into the main tube, the volume being made up to 50 ml. The tube is

[1] *Cf.* A. P. Sy, *J. Franklin Inst.*, 1903, **155**, 171.
[2] *Cellulosechem.*, 1933, **14**, 43.
[3] *Tidsskrift for Søvaesen*, 1928, **99**, 407.
[4] *Z. ges. Schiess- u. Sprengstoffw.*, 1910, **5**, 47.
[5] *Int. Congr. Appl. Chem.* VIII., 1912, Vol. 4, Section III. (*b*), 147.
[6] *Ind. Eng. Chem.* (*Anal.*), 1932, **4**, 77.
[7] *Z. angew. Chem.*, 1904, **17**, 982, 1018, 1074.

well shaken and the contents filtered. A little permanganate is added to oxidize nitrous acid, and the nitrogen is estimated by the Schulze-Tiemann method. Titration with alkali has also been used to determine the nitrous and nitric acid, but in this case allowance must be made for the calcium carbonate in the nitrocellulose.

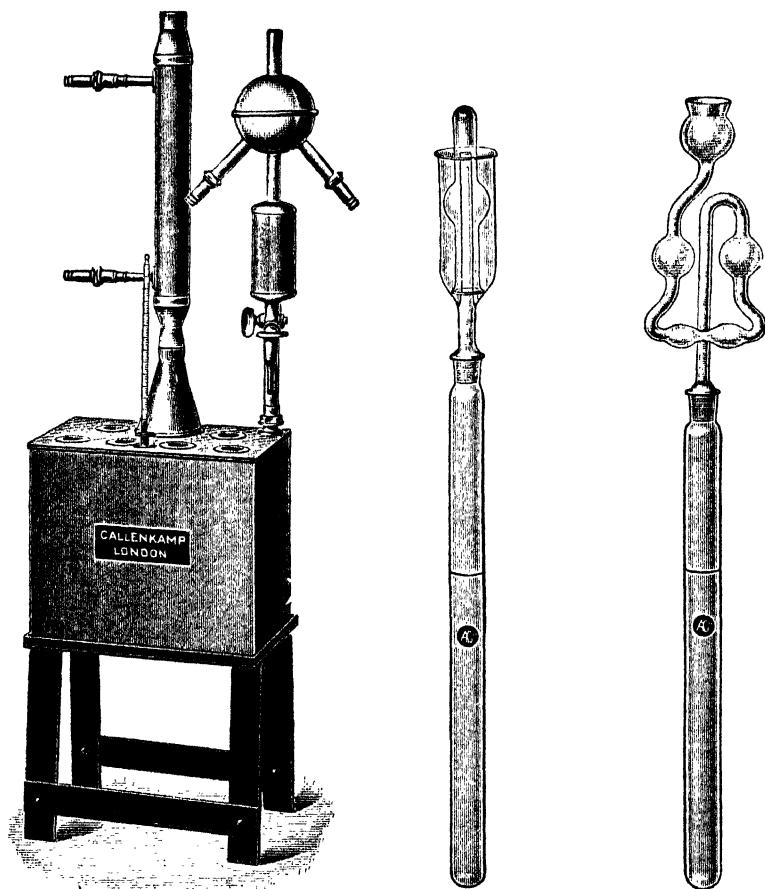



FIG. 124.

The test has generally been found very reliable.[1] Sometimes rapid decomposition sets in and the test has to be discontinued; occasionally explosions occur. For this reason a modified test has been devised by V. Meerscheidt-Hüllessem [2] in which the reaction tube can be rapidly cooled without removing it from the bath.

[1] Lenze and Pleus, *Z. ges. Schiess- u. Sprengstoffw.*, 1919, **14**, 298; *Reichsanstalt, Ann. Rept.* VI., 1927, 128; VIII., 1930, 28; de Bruin, *Rec. trav. chim.*, 1921, **40**, 644; *Communiqué de la Sté Anme Fabr. Néerl. d'Expl.*, No. 5.

[2] *Z. ges. Schiess- u. Sprengstoffw.*, 1935, **30**, 75.

A modification of the test is described by Mayrhofer.[1] In this the nitric peroxide is collected in potassium iodide solution, which is then titrated with thiosulphate. A special feature of the modified method is the addition of 0·05 to 0·25 ml. of water to the 2 g. of explosive, to facilitate hydrolysis of the esters. Comparative tests are carried out under the wet and dry conditions. The method is stated to be applicable to nitroglycerine powders.

The Bergmann and Junk test is applied to nitrocellulose powders in Germany.[2] 5 g. of powder is taken for the test, and parallel tests are made on a control powder. A good nitrocellulose powder with stabiliser is stated to give 5 to 8 ml. of nitric oxide after five hours' heating.

VI. Loss of Weight due to Decomposition

(a) Method of Sy [3]

The unground powder is heated at 115° on an open dish for eight hours daily for six days. The daily loss of weight is determined. Limits are given for nitrocellulose powders of different thicknesses. The test has been criticized on the ground that the volatile catalysts do not exert their due influence, and further, that different powders in the same oven may affect one another. Somewhat analogous tests are described by Jacqué [4] and Berkhout.[5]

(b) Method of Meerscheidt-Hüllessem [6]

In this test 10 g. of the unground powder is heated in a glass tube to retain the volatile catalysts. The tubes are 200 mm. long and 30 mm. in diameter and are maintained for eight hours each day at 115° in a bath capable of holding a large number of tubes. The samples are weighed every day up to about ten days.

(c) Dutch Test [7]

Thomas's original test (p. 568) has been gradually developed, and has taken the form of a " Loss of Weight " test. In this form it has

[1] *Z. ges. Schiess- u. Sprengstoffw.*, 1918, **13**, 425, 448; see also Will, *ibid.*, 1919, **14**, 61; Tonegutti, *ibid.*, 1927, **22**, 257; Metz, *ibid.*, 1932, **27**, 150; Wiggam and Goodyear, *Ind. Eng. Chem.*, 1932, **24**, 72.

[2] Kast-Metz, *Chem. Unters. d. Spreng- u. Zündstoffe*, 312; *cf.* Becker and Hunold, *Z. ges. Schiess- u. Sprengstoffw.*, 1932, **27**, 79.

[3] *J. Amer. Chem. Soc.*, 1903, **25**, 549; *cf.* also Escales, *Z. angew. Chem.*, 1905, **18**, 940.

[4] *Z. ges. Schiess- u. Sprengstoffw.*, 1906, **1**, 395. [5] *Ibid.*, 1922, **17**, 33.

[6] *Z. ges. Schiess- u. Sprengstoffw.*, 1926, **21**, 137.

[7] *Z. angew. Chem.*, 1927, **40**, 991; *cf.* Stettbacher, *Z. ges. Schiess- u. Sprengstoffw.*, 1929, **24**, 176.

received considerable attention in Holland for smokeless powders. The apparatus consists of a glass tube 160 mm. long and 18 mm. internal diameter, with a glass stopper. 4 g. of the powder, finely ground and passed through a 0·5 mm. sieve, is placed in the tube, which is then heated at 104° to 106° for nitroglycerine powders and 109° to 111° for nitrocellulose powders. The tube remains open for the first eight hours, but is closed during each subsequent heating. The sample is weighed every morning and evening. Stable powders should not lose more than 2 per cent. from eight to seventy-two hours.

(d) Brunswig's Test[1]

5 g. of powder is heated in an open glass dish in an oven of special construction fitted with a revolving stand. The loss of weight is determined, first after three days' continuous heating at 110°, and then after daily periods of eight hours. Comparisons of this test with other stability tests are given by Metz.[2]

VII. Gasometric Stability Tests

(a) Will Test[3]

This is used as a rule only for ungelatinized nitro-cotton. It is a valuable test for the control of the manufacture, but requires considerable attention and somewhat elaborate apparatus. The nitro-cotton (2·5 g.) is heated at 135° in a current of carbon dioxide. The heating tube is fitted with a glass spiral to pre-heat the carbon dioxide, before it reaches the explosive. The oxides of nitrogen evolved by the explosive are carried forward by the carbon dioxide, passing through a copper U-tube containing copper and copper oxide, which is maintained at a red heat. All oxides of nitrogen are thus reduced to nitrogen, whilst carbon monoxide and hydrogen are converted to carbon dioxide and water. The gases are then led into a gas-measuring tube filled with potassium hydroxide solution. This absorbs the carbon dioxide, and leaves the nitrogen, which is measured at intervals of fifteen minutes for four hours. The heating tubes are enclosed in a metal case with strong glass windows, as explosions occur occasionally. A good nitro-cotton gives a uniform evolution of gas, whilst unstable nitro-cottons give an irregular and increased evolution. Purity of the

[1] Brunswig, *Das rauchlose Pulver*, p. 399.

[2] *Z. ges. Schiess- u. Sprengstoffw.*, 1932, **27**, 150.

[3] *Mitt. aus der Zentralstelle*, Heft 2, 1900; Heft 3, 1902; *Z. angew. Chem.*, 1901, **14**, 743; *cf.* Robertson, *J. Soc. Chem. Ind.*, 1902, **21**, 819.

carbon dioxide is of importance. A special apparatus for this purpose has been described by Farmer.[1]

A modification of the test has been described by Goujon [2] in which the heating tube is enlarged to hold 10 g. of nitro-cotton.

A similar test on a smaller scale is described by Berl and Kunze.[3] The quantity of nitrocellulose is reduced to 0·3–0·5 g. An electrically heated copper block is used in place of a liquid bath.

As all volatile substances are driven off by the current of gas, the Will test measures essentially the decomposition due to non-volatile catalysts such as traces of sulphuric acid.

(b) Dupré's Vacuum Test [4]

1 g. of the ground dried powder is placed in the test-tube. The top of the tube ends in a flat ground surface, and the joint is made between this and a similar flat surface of the connecting tube by means of luting composition. A similar joint is made to the manometer which consists of a syphon barometer. The bath is kept at a constant temperature, *e.g.* 125°, by boiling water under increased pressure. The evacuated tube is placed in an orifice in the bath. After half an hour the tube is re-evacuated and the test started five minutes later. Readings of the manometer are then taken every half-hour for about four hours. The tubes can be re-evacuated if necessary.

(c) Mittasch's Method [5]

The chief feature of this test is that the rise in pressure of the gases is registered automatically. This necessitates more complicated apparatus, and the practical application of the test has been very limited.

(d) Obermuller's Method [6]

In this test the explosive is heated in a vacuum, and the gas evolved is measured by means of a mercury manometer. Various forms of the test have been described. In one of these 1 to 2 g. of nitro-cotton are placed in a tube of 12 ml. capacity which is heated at 135° or 140°. A small glass rod rests on the nitro-cotton to prevent it from being ejected upwards on application of the vacuum. Useful results have

[1] *J. Chem. Soc.*, 1920, **117**, 1446.

[2] *Mém. de l'Artill. Franç.*, 1929, **8**, 897.

[3] *Z. angew. Chem.*, 1932, **45**, 669.

[4] *Ann. Repts. of H.M. Insp. Expl.*, 1903, p. 27; 1904, p. 28.

[5] *Z. angew. Chem.*, 1903, **16**, 929.

[6] *Berlin Bezirksverein der Verein deutscher Chemiker*, 1904, 30; *J. Soc. Chem. Ind.*, 1905, **24**, 347; *cf.* also Willcox, *J. Amer. Chem. Soc.*, 1908, **30**, 271; *Z. ges. Schiess- u. Sprengstoffw.*, 1908, **3**, 246; Pleus, *ibid.*, 1910, **5**, 121; Lenze and Pleus, *ibid.*, 1919, **14**, 315.

been obtained for ungelatinized nitro-cotton, but the test appears to be unreliable for gelatinized powders after storage. This is probably due to the continuous removal of the volatile catalysts.

(e) Brame's Method [1]

This also depends on the measurement of the rise of pressure in an evacuated tube containing the explosive, by means of a mercury manometer.

(f) Chiaraviglio and Corbino [2]

These authors describe a method in which a very sensitive manometer is used to measure the rate of decomposition at relatively low temperatures. Volmer [3] has described a method based on the same principle.

(g) Taliani's Test [4]

This test has a device which prevents the volatile products from reaching the cool parts of the apparatus, thus ensuring that the catalysts are kept in contact with the explosive, and also preventing the distillation of nitroglycerine, when this forms a constituent of the explosive. The apparatus is shown in Fig. 125. The tube A containing 1·3 g. of the explosive is fitted with a tap C, and connected with a tube which has a double bend B. The U-shaped part of this tube is partly filled with heavy paraffin. This part of the apparatus is entirely enclosed in the hot bath. The tube B is further joined by a rubber connection to a glass tube leading to the manometer F. One limb of the manometer is divided into two tubes, one of which is fitted with a tap as shown. The paraffin trap prevents the volatile products from entering the manometer.

The test is usually carried out at 120° with nitroglycerine powders and 135° with nitrocellulose. The tap C and the manometer tap remain open until equilibrium has been obtained in the whole apparatus and any moisture has evaporated. When the taps are closed, any gases evolved from the explosive exert a pressure on the paraffin. By raising the mercury reservoir, the paraffin can be

[1] *J. Soc. Chem. Ind.*, 1912, **31**, 159.

[2] *Atti R. Accad. Lincei*, 1915, **24**, 5*a*, 120; *cf.* de Bruin, *Communiqué de la Sté. Anme. Fabr. Néerl. d'Expl.*, No. 5.

[3] *Z. angew. Chem.*, 1921, **34**, 151.

[4] *Rivista d'Artigliera e Genio*, 1921, vol. i.; *Gazz. Chim. Ital.*, 1921, **51**, I, 184; *cf.* also Tonegutti, *Annali. Chim. Appl.*, 1925, **15**, 542; *Z. ges. Schiess- u. Sprengstoffw.*, 1926, **21**, 81, 127; Goujon, *Mém. de l'Artill. Franç.*, 1929, **8**, 837, 902; *Z. ges. Schiess- u. Sprengstoffw.*, 1931, **26**, 217, 261, 289, 330, 362, 400; de Bruin, *Communiqué de la Sté. Anme. Fabr. Néerl. d'Expl.*, No. 5, 1927; Wiggam and Goodyear, *Ind. Eng. Chem.*, 1932, **24**, 72.

brought to the same level in the two limbs. The pressure is then read off on the scale. Readings are taken every five minutes until the difference of pressure reaches 100 mm. or 300 mm. Good drying of the explosive is necessary, as the results are affected by moisture. Calcium carbonate also has a marked effect.

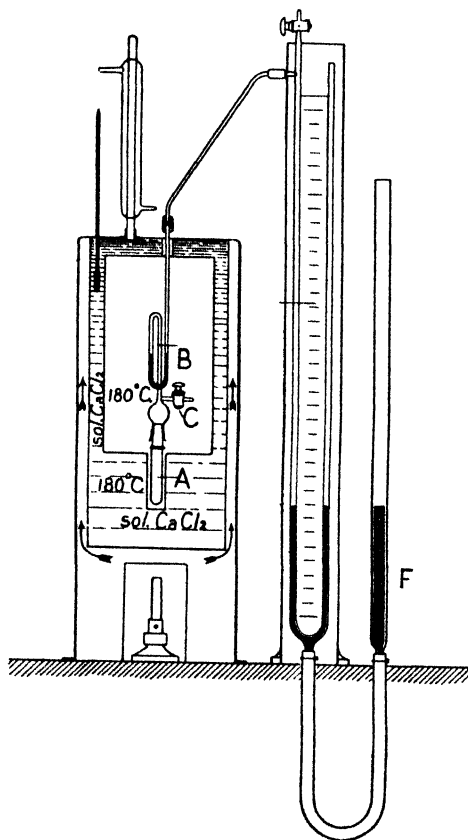



FIG. 125.

(h) V. Meerscheidt-Hüllessem's Test[1]

One of the main features of the test of Taliani described above is that the volatile products are not allowed to escape. This can also be effected by enclosing the powder in a vessel containing liquid paraffin with a syphon tube arranged so that the gases evolved displace the liquid and cause it to overflow into a beaker which can be periodically weighed. The test is carried out at 120° with measurements every fifteen or thirty minutes. The method is simple, but very few results have been published so far.

[1] *Z. ges. Schiess- u. Sprengstoffw.*, 1933, **28**, 6.

(i) Desmaroux Test [1]

A copper bath is filled with glycerine and maintained at constant temperature by a regulator. It is double walled to conserve the heat and has a number of orifices to receive the glass heating tubes. These are 3 cm. in diameter and 10 cm. high. Each tube has a ground-glass stopper with a capillary outlet leading to a mercury manometer. 10 g. of explosive is placed in the tube, which is then evacuated. The tests are carried out at 75° and 108·5° and the rate of decomposition is measured by the rise of pressure in the manometer.

(j) Marqueyrol's Test [2]

The explosive is heated at 50° in a vacuum, and the slow evolution of gas is measured by means of a manometer. Readings are taken every three or four days over a long period.

VIII. Measurements of Acidity

One of the primary causes of instability of nitrocellulose and gelatinized explosives is the presence of traces of acidity, or of unstable esters which readily break down, yielding acids. Since esters are hydrolyzed by moisture in presence of acids, the decomposition is autocatalytic, and the presence of acid is thus of great importance.

(a) Angeli's Test [3]

This is designed primarily for gelatinized powders. The powder is ground or cut into very thin flakes and 0·5 g. placed in a test-tube. A small quantity of distilled water is added, and then 3 or 4 drops of a 0·2 per cent. alcoholic solution of dimethylaminoazobenzene. The whole is well mixed and either warmed for a few moments in boiling water or allowed to stand in the cold. The solid powder takes up the indicator and becomes more or less red according to its degree of acidity.

(b) Tomonari's Test [4]

This test is applied to ungelatinized nitrocellulose. It depends on the solubility of acidic impurities of the nitrocellulose in methyl alcohol. 1 g. of the nitrocellulose is boiled for fifteen minutes with methyl alcohol and the solution is titrated with 0·01 *N* sodium

[1] *Mém. Poudres*, 1926, **22**, 245. [2] *Ibid.*, 1928, **23**, 178.

[3] *Atti R. Accad. Lincei*, 1918, **27**, 164; *Z. ges. Schiess- u. Sprengstoffw.*, 1922, **17**, 115; *cf.* Giua, *Chimica della Sostanze Explosive*, 1919, 472.

[4] *Z. angew. Chem.*, 1934, **47**, 47.

hydroxide solution, using methyl red as indicator. The titre is called the acid number (x), and $100/x$ is called the *stability number*. The explosion temperature falls with a rise in the value of x. When x is less than 5 the cellulose nitrate is considered stable.

(c) Measurement of pH Value

This method depends upon extraction with water and measurement of the acidity either by indicator solutions or by the quinhydrone electrode.[1]

It is necessary to use pure water, as used for electric conductivity work, and to adhere to constant conditions of working. The method is frequently combined with a heating trial. Thus Hansen [2] heated smokeless powders in the ground condition at 110° and tested samples at intervals of an hour by means of the quinhydrone electrode to ascertain the rate of formation of acid. In a modified method the powder is heated under water at 100° to bring about a hydrolytic decomposition. Grottanelli [3] passes a slow current of air over a large sample (500 g.) of powder, which is maintained at 80°, and then into an absorption vessel in which the pH value is measured. Pavlik [4] also passes the gases into water under modified conditions. The effect of calcium carbonate in powders has been examined by Metz.[5]

(d) Conductivity Method

De Bruin and de Pauw [6] have described a method depending on the electrolytic conductivity of an aqueous extract of the explosive. A number of flasks, each containing a weighed quantity of dried nitrocellulose or powder, are first heated to drive off residual moisture. The contents of one of the flasks are treated with 150 ml. of "conductivity water," well shaken, and allowed to stand. The flask is again shaken, the liquid is filtered, and its conductivity measured. The other flasks are heated at constant temperature (100° to 132°) for known periods and the conductivity is similarly determined. The conductivity increases with the duration of the heating, and this increase is taken as a measure of the stability.

[1] *Cf.* Marshall, *Explosives*, vol. iii., p. 215; *Rev. gén. mat. plastiques*, 1937, **13**, 79; A. Kubferach, *Z. ges. Schiess- u. Sprengstoffw.*, 1936, **31**, 327.

[2] *Dansk Artilleritidskrift*, 1925, **12**, 129.

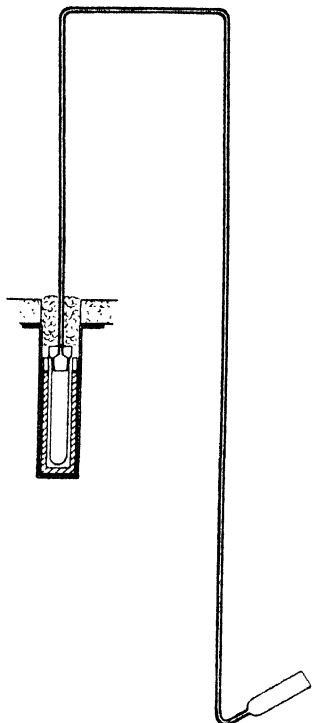
[3] *Mém. R. Accad. d'Ital.*, 1931, **11**, No. 6, 5.

[4] *Chim. et Ind.*, 1933, **29** (Special No.), p. 978; *cf.* Déribéré, *Rev. gén. mat. plastiques*, 1934, **10**, 260.

[5] *Z. ges. Schiess- u. Sprengstoffw.*, 1934, **29**, 361.

[6] *Communiqué de la Sté. Anme. Fabr. Néerl. d'Expl.*, No. 6, 1927; *Z. ges. Schiess- u. Sprengstoffw.*, 1929, **24**, 185.

IX. Stability of High Explosives

The aromatic nitro-compounds, which form the basis of most of the high explosives used for Service purposes, do not as a rule respond readily to such tests as the Abel heat test. In general these compounds undergo very little deterioration on storage, but in some cases it is necessary to test them. The most reliable results of definite value in the comparison of high explosives are obtained by vacuum stability tests.

Vacuum Stability Test[1]

The explosive is dried and weighed out into a test-tube of the pattern shown in Fig. 126. The manometer is attached and the tube evacuated and placed in a thermostat of special design. The temperature of the test varies from 80° to 180° according to the explosive under test. The progress of the decomposition is followed by readings of the mercury manometer.

Examples of the gas evolution from a number of explosives are given by Robertson.[2]

Fig. 126.

Method of Haid, Becker and Dittmar[3]

The apparatus consists of a glass vessel connected with a manometer. The explosive is dried over phosphorus pentoxide, and 42 g. introduced through a side-tube which is then sealed off. The manometer is in the form of a U-tube and contains mercury covered with a layer of paraffin. The glass vessel is also fitted with a side-tap. It is heated in a bath to 75° and completely sealed. The evolution of gas is then measured by means of the manometer.

Acidity Measurements[4]

The method of *p*H determination is applied as in VIII (*c*) above (p. 579). 5 g. of explosive is heated at temperatures ranging from 75° to 132° according to the nature of the explosive, and the gradual fall of *p*H is measured by periodic tests.

[1] Farmer, *J. Chem. Soc.*, 1920, **117**, 1432, 1603; 1922, **121**, 174.
[2] *J. Chem. Soc.*, 1921, **119**, 13.
[3] *Z. ges. Schiess- u. Sprengstoffw.*, 1935, **30**, 66.
[4] Metz, *Z. ges. Schiess- u. Sprengstoffw.*, 1929, **24**, 335.

Loss of Weight

In Germany, industrial blasting explosives are exposed to a temperature of 75°. 10 g. is heated in a loosely covered weighing bottle, 30 mm. diameter and 50 mm. high, and the loss of weight is determined periodically.

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MATCHES AND FIREWORKS

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A. MATCHES

I. NATURE OF MATERIAL FOR MATCH-STEMS

1. Woods

WHITE or soft pines of Canadian origin are largely used in the manufacture of matches. The pine tree grows to a height of 100 ft. or more, and is 7 ft. or more in diameter. For the manufacture of matches the young pine, on account of its very soft texture, is to be preferred. It is essential to have the wood dry and thoroughly seasoned, thereby reducing the water content and improving its physical properties by rendering it less brittle. The wood should be stored in well-ventilated sheds and protected from the sun and rain.

In addition to pine, fir and spruce, the following woods are used, especially in countries to which these are indigenous, viz.: aspen, poplar, lime, beech and willow, and to a more limited extent, alder-wood. Aspen wood, which comes mainly from Russia, is very easy to flake and gives splints of uniform size. The strips of wood for match-boxes are also made from the aspen tree and on the same machine. It is probable that for match splints aspen wood will supplant pine wood in this country.

Fir woods closely resemble the pines in being needleleaf or soft woods but have no resin ducts. The variety mostly favoured is the white or silver fir.

Spruce woods resemble the soft pines. They grow extensively in North America and Europe. The common varieties are the Norway spruce (*Picea excelsa*) and the Douglas spruce or fir (*Pseudotsuga douglasii*). The Norway spruce resembles silver fir but the resin ducts are visible though few in number.

2. Wax Matches or Vestas

The stem of wax matches consists of a wick of twisted cotton threads, coated with wax, or more generally with mixtures of stearin, paraffin, and gum dammar or gum opal. These matches burn for a longer time than matches made from wood.

3. Cardboard Matches

Within recent years safety-matches with stiff paper or cardboard stems have become very popular, and numerous patents have been taken out for the manufacture of such matches, *e.g.* B.P. 288620/1927 and B.P. 332700/1929. These are usually made up in the form of a book, and generally consist of two rows of ten matches each in a cover. These matches are made automatically by machinery. The cardboard is slit and dipped, and the composition then put on the cover. The machine also binds and cuts the books apart. Matches are also produced in disc form [1] and in the form of a cylinder. When a match is withdrawn from the latter bundle it is ignited by friction. Various details of paper matches are described in U.S.P. 2022088 (1936). Hand dipping in batches still survives to some extent in cardboard match manufacture.

II. Substances used to Impregnate the Splints

The match sticks are either square or round, according to whether they are made by flaking or planing. The grooved splints, sometimes employed, are punched by upward cutting dies from small wooden blocks fed into the machine in a special way. The round splints are compressed, and have a closer texture than the square sticks, and are better suited for sulphur-coated match manufacture. The sulphur which coats the lighting end does not enter the pores, so that a loose structure is unnecessary. With the majority of other dipping substances it is preferable to have a porous foundation, as the substances tend to penetrate the wood. Sulphur is now scarcely ever used. Paraffin and other waxes are generally employed to impregnate the splints. In addition resin and other fatty acids such as stearic are commonly employed.[2] These will be considered individually. To prevent the after-glow of the splints, and the falling-off of the glowing ember, the splints are dipped into a solution of phosphoric acid and ammonium nitrate, or other fire-proofing materials, such as alum or boric acid. Hygroscopic substances should be avoided.

A solution of celluloid in amyl acetate may be used in place of gum, etc., as binder in order to render the match damp-proof.[3] The stems and heads may be dipped in a similar solution. A moisture-proof match-ignition composition containing cellulose derivatives has also been suggested in other patents (*e.g.* 355901/1930).

1. Paraffin and Other Waxes

Waxes, which are usually the fatty esters of the monohydric alcohols, find a limited application in the match industry. Paraffin wax, a

[1] B.P. 304883/1927. [2] Austr. Pat. 144644 (1936). [3] B.P. 322545/1928.

hydrocarbon, is the most important in this connection. It is the highest boiling fraction of the products of distillation of paraffin and lignite. It is sold in different grades according to its melting point, which may range from 35° to 60° C. For the manufacture of matches the more or less yellow and brown, soft, scaly variety is the most important. Paraffin waxes with a melting point of 98° to 102° F. (Scotch method), 101° to 105° F. (American method), and 38° to 39° C. (German method) are the most favoured.

The determination of the melting point of wax may be carried out as follows: 0·5 g. is weighed approximately (first time, afterwards judged by size) and wedged at the top of a hook of platinum wire (0·025 in. diam.) fused on to the end of a glass rod, which passes through a hole in the cork fitted into a dry test-tube. The cork also carries a thermometer with its bulb near the platinum hook. The test-tube is slowly heated in water and the melting point noted. Alternatively, the wax may be melted in a small beaker, slowly stirred with a thermometer, until the temperature becomes steady for a short period, with solidification of the mass. For more accurate determination a large bath is employed and the liquid mechanically stirred. When the melting point is not sharp and for petroleum jellies the apparatus of Ubbelohde may be employed. A small quantity of the jelly is pressed into a small glass perforated cup which fits on to the bulb of the thermometer. On slowly heating, the temperature at which the drops of liquefied paraffin fall away from the cup is noted.[1] The English method of determining the setting point of paraffin wax consists in filling a test-tube (1 in. diam.) to a depth of 2 in. with molten paraffin and inserting a small accurate thermometer. The tube is then allowed to cool and the temperature at which the thermometer remains stationary for a short period is regarded as the setting point.

Shukoff's apparatus for determining the titre test of fatty acids consists of a tube 3 cm. diam. surrounded by a Dewar vacuum mantle, the outer diameter of which is 5 cm. and the height 10 cm. The molten paraffin is poured into the inner tube, which is closed by a cork fitted with an accurate thermometer. The vessel is slowly cooled with shaking and the point at which without further shaking the thermometer remains steady and then rises is noted. The highest point is taken as the setting point. *The Institute of Petroleum Technologists' Handbook* (1929) describes a standard apparatus for the setting point determination of paraffin wax.

Considerable uncertainty still exists as to the manner in which the English, Scotch, American and German methods of examination are carried out. The German and American methods are in close agreement when Fahrenheit degrees are converted into Centigrade degrees

[1] See Reilly and Rae, *Physico-Chemical Methods*, Chap. xix., London, 1940.

by the well-known formula $C^\circ = (F^\circ - 32) \times \frac{5}{9}$; whereas after converting the English or Scotch degrees by the same formula, it is always necessary to add on 2° C. Ignorance of this difference in the methods is often taken advantage of by dealers, as paraffin wax is sold according to melting point, and the German test gives higher results.

The wax commonly used when first obtained is yellow; if melted and poured into cold water, it forms thin strips which are bleached white by the action of the air. In this country, wax for the manufacture of wax matches has been partly or entirely replaced by stearin with or without paraffin wax. Cotton threads or bobbins are passed through a ring so as to form one single thread, which is then passed through a trough containing the molten wax mixture. This thread is then passed through a wire-drawing plate which gives it an exactly cylindrical shape and a smooth surface. The wax mixture used usually contains about 10 to 15 per cent. of paraffin wax. Wax matches for tropical countries contain a small amount of Carnauba wax. The latter is a hard vegetable wax which raises the melting point and increases the hardness of the wax, thus preventing the matches from sticking together.

In impregnating the splints with paraffin wax the molten paraffin is heated to such a point that a match stick "boils" when plunged into it. As the vapour of paraffin wax is unpleasant, it is desirable to fit an efficient air draught to the paraffin bath.

2. Stearin (Stearic Acid)

Stearic acid, incorrectly called stearin, is one of the higher fatty acids. It is a waxy, crystalline solid, which melts at 69·2°. It is made on an industrial scale from animal and vegetable fats. These are hydrolysed by means of superheated steam alone or with addition of a small percentage of calcium hydroxide. The calcium salt produced is changed into stearic acid by the addition of the requisite amount of sulphuric acid.

Stearin was used, at one time, with the addition of a little resin, in the preparation of the wood for matches "de luxe." In the manufacture of matches it is unnecessary to use the hardest and whitest sorts of stearin, as the softer kinds have been found to give even better results. Stearin has been replaced by paraffin for making wood matches, but it is still used, with gum opal or dammar, for wax match stems. In the match industry the only test required is to determine the melting point of the stearin before use. In this connection the Shukoff method for determining the melting point of paraffin wax (*cf.* p. 584) is used.

3. Resin

The dried resin of the Coniferæ is used in match compositions, or for mixing with the stearin ; Venice turpentine is the best. Addition of resin causes the flame to smoke strongly. The addition of insoluble synthetic resins as binding material is claimed to give a match-head unaffected by water.[1]

4. Sulphur

For occurrence, examination for purity, etc., see Vol. I., p. 358 *et seq.*

Sulphur melts at 114·5° to a clear yellow liquid, which, on further heating to above 125° becomes darker and very viscid ; at 400° it is again yellow and mobile and begins to volatilize. During cooling these phenomena reappear in inverse order. If the sulphur becomes thick, it is too hot, and must be cooled further before the splints can be dipped.

For the manufacture of matches very pure sulphur is not needed. The small amount adhering to the splint always appears pure and is inflammable. Finely powdered roll-sulphur is preferred to flowers of sulphur for the manufacture of safety-match compositions.

Differences between Powdered Sulphur and Flowers of Sulphur under the Microscope. The powdered sulphur consists of more or less transparent crystals, while flowers of sulphur consist of dark, cauliflower-shaped masses. In polarized light, between crossed nicols, flowers of sulphur are devoid of optical activity, while the crystalline particles of the powdered sulphur appear light on a dark ground. Sulphur is scarcely ever used as a coating for match splints in this country, although it is an essential ingredient of some match compositions, especially those used for safety-matches.

III. Materials for Match Compositions

A. COMBUSTIBLE SUBSTANCES

1. **Ordinary or Yellow Phosphorus.** — Phosphorus is usually prepared from bones or naturally occurring phosphorite, in both of which it is present as tricalcium phosphate. At ordinary temperatures yellow phosphorus is a crystalline solid having a sp. gr. of 1·83 at 10°. Above 15° it becomes soft and waxy, melting at 44·4° to a yellow liquid. It is readily soluble in carbon disulphide, chloroform, benzene and sulphur chloride (S_2Cl_2), and almost insoluble in alcohol and water. Friction, or warming to 60°, in the air causes phosphorus to burn with a bright, yellowish white flame, to phosphorus pentoxide,

[1] Ger. Pat. 640903 (1937); Swed. Pat. 84455 (1935).

P_2O_5. Yellow phosphorus is a deadly poison, as little as 0·1 to 0·2 g. causing death; inhalation of the "fume" causes "phossy jaw," or necrosis of the jaw-bone, a disease prevalent amongst workers in the match factories. Fortunately, its use in most countries is now prohibited by law.

Examination of Commercial Yellow Phosphorus. The impurities present in yellow phosphorus are traceable to the sulphuric acid used in its manufacture. The principal adulterants are sulphur, arsenic and iron. To test for sulphur, a fragment of the phosphorus is dissolved in dilute nitric acid, and the solution, which now contains the phosphorus as phosphoric acid, is tested with a solution of barium nitrate; a white precipitate, insoluble in nitric acid, indicates the presence of sulphur in the phosphorus. Another portion of the solution is diluted, nearly neutralized with alkali, and treated with sulphuretted hydrogen; any arsenic originally present exists as arsenic acid in the nitric acid solution. The latter with hydrogen sulphide gives a yellow precipitate of arsenious sulphide. If iron is present, a precipitate of Prussian blue is obtained, on the addition of a few drops of potassium ferrocyanide solution to the nitric acid solution.

2. **Dark Red Phosphorus,** a second allotropic form of phosphorus, is manufactured on the large scale by heating the yellow variety in sealed iron cylinders for a few minutes at 250° to 300°. Red phosphorus differs considerably in properties from the yellow form. It is non-poisonous, is unaffected by the air and is insoluble in carbon disulphide. Moreover, it is odourless. It has a sp. gr. of 2·106. When heated in air it does not ignite until a temperature of 200° is reached. Generally it is less chemically active than yellow phosphorus.

Red phosphorus is used chiefly for the preparation of the striking surfaces on safety-match boxes and is also occasionally employed in the manufacture of "strike anywhere" match compositions. While pure red phosphorus is non-poisonous, the commercial product can act as a poison, as it frequently contains traces of the white modification. Fresenius and Luck[1] analysed a sample of commercial red amorphous phosphorus with the following results:—

Red phosphorus	92·630 per cent.
White phosphorus	0·560 ,,
Phosphorous acid	1·302 ,,
Phosphoric acid	0·880 ,,
Water and impurities	4·662 ,,

Although the presence of a small amount of white phosphorus is not in itself detrimental in match-making, it has been assumed to be

[1] *Z. anal. Chem.*, 1872, 11, 63.

the cause of a slow oxidation to phosphorous and phosphoric acids, which on account of their acid and hygroscopic properties, act on the other substances present. This supposition is, however, unnecessary, for red phosphorus, which has been carefully purified, becomes oxidized after long contact with air, and contains under these circumstances considerable quantities of phosphorous acids. Factories do not generally trouble about any special examination or purification, although in 1909 it was proposed to use "neutral amorphous phosphorus" obtained from the ordinary product by purification methods. The phosphorous acids are estimated quantitatively by extracting a weighed quantity (10 g.) on a filter with warm water, until the filtrate no longer reacts acid. A definite portion of the filtrate is now oxidized by repeated evaporation with nitric acid, and the total phosphoric acid then precipitated with magnesia mixture in the usual way (*cf.* Vol. III., p. 519). The phosphorous acid is estimated with mercuric chloride in another portion of the filtrate. To estimate the percentages of white and red phosphorus present, Fresenius and Luck (*loc. cit.*) oxidize the phosphorus, after washing free from acids with warm water, with fuming nitric acid to phosphoric acid, and estimate the amount of phosphorus in this as magnesium ammonium phosphate. The quantity of red phosphorus is similarly estimated in another portion of the sample, after extracting the yellow variety with carbon bisulphide. The difference between these two quantities gives the amount of white phosphorus present.

The German official method, worked out by Siemens, is as follows: 3 g. of phosphorus is dried, and boiled for half an hour on a steam-bath, under a reflux condenser, with 150 ml. of benzene, and filtered. 1 ml. of this solution is added to 1 ml. of a solution of ammoniacal silver nitrate, made up by dissolving 1·7 g. of silver nitrate in 100 ml. of ammonia of sp. gr. 0·922. If, after shaking and allowing to stand, no change or only a yellow coloration of the aqueous solution takes place, white phosphorus is absent. But if the aqueous solution is coloured red or brown or contains a black or brownish-black precipitate, white phosphorus is present. The colour of the aqueous solution should be judged directly after shaking and allowing to stand, and not after prolonged standing.

3. **Light Red Amorphous Phosphorus**, sometimes called scarlet phosphorus, is another allotropic form. It is prepared by dissolving yellow phosphorus in phosphorus tribromide and boiling the solution. The new modification separates out of the solution as a finely divided, amorphous powder. Like dark red phosphorus, the scarlet form is not poisonous. It is, however, more chemically reactive than the former owing to its more finely divided condition. Conversion of scarlet into dark red phosphorus may be brought about by continued

heating at 300° in a current of carbon dioxide. Schenck determines the phosphorus by heating a weighed quantity with water, together with bromine contained in a small tube, in a scaled tube, for two or three hours in a steam-bath at 100°; the oxidized phosphorus is weighed as magnesium pyrophosphate.

Scarlet phosphorus is used in compositions for parlour matches, *i.e.* matches requiring no special ignition surface.

4. **Phosphorus Sesquisulphide (P_4S_3).**—This compound is formed by slowly heating the calculated quantities of phosphorus and sulphur in a current of carbon dioxide at 330°; a small excess of sulphur is used. By sublimation at 260°, regular crystals are obtained, but on crystallization from carbon disulphide, rhombic prisms melting at 166° and boiling at 380° are obtained. Phosphorus sesquisulphide is soluble in carbon disulphide, phosphorus trichloride and in aqueous solutions of sodium and potassium sulphides. Alkalis readily decompose it. The commercial product ignites in air at 98° to 99°. Cold water has no appreciable action on phosphorus sesquisulphide, but boiling water decomposes it into sulphuretted hydrogen and phosphorous acid. The commercial product sometimes contains free phosphorus, the presence of which is detected by passing a current of hydrogen over the sulphide when, if phosphorus is present, the issuing gas will burn with a green flame. The pure product keeps well in stoppered bottles, but the commercial product gradually decomposes with evolution of sulphuretted hydrogen.

Phosphorus sesquisulphide was officially introduced into France by Sevène and Cahen [1] for the manufacture of "strike anywhere" matches, free from white phosphorus. It is now used in the manufacture of matches almost to the exclusion of yellow phosphorus.

The examination of phosphorus sesquisulphide is carried out first, by the smell (odour of phosphorus) and then by Mitscherlich's test (*cf.* detection of phosphorus in match-heads, p. 622), or by the method of Schenck and Scharff. These methods are exact and permit the detection of very small traces.

5. **Lead Thiosulphate (PbS_2O_3)** is now used for the preparation of match compositions, which ignite on any surface. It is prepared by treating a solution of "sugar of lead" (lead acetate) with sodium thiosulphate; it is a pure white, inodorous, tasteless powder, insoluble in water and not hygroscopic. It should be kept in well-closed bottles. 12 kg. of lead acetate yield, when treated with 5 kg. of sodium thiosulphate, about 9·5 kg. of lead thiosulphate. A pure sample should contain no water-soluble matter.

6. **Antimony Trisulphide (Sb_2S_3)** is used to some extent for match compositions, but principally in the preparation of the striking surface

[1] Ger. Pat. 101736/1898.

of safety-match boxes. It can be obtained in a purity of 99 per cent. Tests for purity are not necessary.

7. **Other Substances.**—A few other substances have been recommended for match compositions, such as persulphocyanic acid, ferrocyanogen compounds, potassium xanthate, thiocyanates, "sulphocuprobarium polythionate" and "thiophosphit." Thiophosphites made by heating such sulphides as antimony and zinc sulphides with red phosphorus and sulphur in an atmosphere of carbon dioxide to a temperature of 450° are used in match compositions patented by the Elektron Fabrik.[1] Matches of this composition are less affected by moisture than those containing phosphorus sulphides. The addition of an ignition mass containing an inorganic non-combustible binding substance has been suggested for repeat ignitible matches.[2]

B. SUBSTANCES WHICH SUPPLY OXYGEN

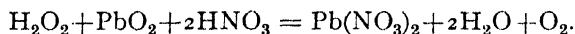
1. **Minium or Red Lead (Pb_3O_4)** is prepared by heating yellow lead oxide (massicot) in air to about 300°, when it absorbs oxygen and becomes converted into red lead. It has a sp. gr. of about 8·8. As the use of minium is solely dependent on its oxygen content, only the purest product should be used (with not more than 1 per cent. of impurity). This is tested by dissolving 1 g. in a mixture of 2·5 g. of nitric acid (sp. gr. 1·15), 3 to 4 g. of water and 0·5 g. of oxalic acid and filtering.

2. **Lead Peroxide mixed with Lead Nitrate.**—This "mixture" is prepared by treating minium with nitric acid of sp. gr. 1·384. A moderate amount of heat is evolved. Minium, whose composition may be written $2PbO \cdot PbO_2$, gives up the lead oxide (PbO) to the nitric acid to form lead nitrate, the peroxide remaining unchanged. Excess of nitric acid is to be avoided, as it not only acts on the binding substance in the match composition, but also renders the phosphorus inactive, by oxidizing it to phosphoric acid. It also gives the mixture a thin consistency, whereas if the correct quantity of acid is used, the product is stiff and pasty. A badly made mixture contains too much lead nitrate, which causes the match-head to sweat, thereby producing a bad ignition and giving an unsightly appearance to the match-head. The product must also be free from lead chlorides and lead sulphate, which are avoided by using pure raw materials.

3. **Lead Peroxide** is prepared from red lead, by boiling it, in fine powder, with dilute nitric acid, washing and drying. It has a sp. gr. of 9·4. It readily parts with oxygen to other substances and hence is used in match compositions. The percentage of lead peroxide in a sample can be estimated by treating the peroxide with a measured

[1] Ger. Pat. 153188. [2] Swed. Pat. 83904 (1935).

volume of hydrogen peroxide previously acidified with nitric acid. The following reaction takes place :—

$$H_2O_2+PbO_2+2HNO_3 = Pb(NO_3)_2+2H_2O+O_2.$$

The undecomposed hydrogen peroxide is then determined by titration with potassium permanganate solution.

4. **Lead Nitrate** is readily obtained in match factories by allowing the wash-waters, obtained in the preparation of lead peroxide, to crystallize.

5. **Manganese Dioxide.**—The tests are fully described in Vol. II., p. 163. The value of the dioxide depends on the amount of available oxygen. Manganese dioxide is seldom used for phosphorus compositions, but is employed for safety and non-poisonous "strike anywhere" match pastes, and also on the striking surfaces.

6. **Potassium Chlorate.**—This is examined as described in Vol. I., p. 618. It is the most powerful oxidizing agent used in the match industry, and the substitution of the very hygroscopic sodium chlorate for it is not to be recommended.

7. **Potassium Nitrate.**—For the examination see Vol. II., p. 420. It is essential that refined saltpetre only be used, as the crude salt contains chlorides which are deliquescent.

8. **Potassium Dichromate.**—For tests *cf.* Vol. II., p. 377. It is used in the manufacture of safety-matches, and in very small quantities in the compositions of red phosphorus matches.

9. **Barium Nitrate, Strontium Nitrate.**—These substances are used principally in pyrotechny (see p. 637).

10. **Calcium Orthoplumbate (Ca_2PbO_4)** is a heavy yellowish-red powder prepared by heating calcium oxide and litharge to redness in air. It was first prepared by Kassner and was recommended as a substitute for lead peroxide and lead nitrate, in the manufacture of non-poisonous "strike anywhere" phosphorus matches. Schwiening's[1] composition is used by match-makers, owing to the prohibition of the use of white phosphorus, and contains calcium orthoplumbate, together with potassium chlorate, amorphous phosphorus, friction material, binding and colouring substances. The calcium plumbate appears to act as a negative catalyst on the explosive mixture of potassium chlorate and phosphorus, retarding the explosion, so that only inflammation occurs.

C. SUBSTANCES WHICH INCREASE FRICTION, INERT SUBSTANCES, OR FILLING MATERIALS

Among these substances are powdered glass, pumice stone, sand, chalk, plaster of Paris, pulverized asbestos, siliceous marl, Kieselguhr, powdered quartz, brown umber, Venetian red, zinc oxide and

[1] Ger. Pat. 86203.

pulverized paper moulded with a binder, *e.g.* rubber solution or starch.[1]

These serve, on the one hand, to increase the friction, and on the other to retard the explosion on igniting the match-head, so that the flame has time to act on the other materials, sulphur, paraffin, etc., which propagate the combustion. Brown umber is a variety of clay coloured by the oxides of iron and manganese. Venetian red is ferric oxide, Fe_2O_3, and is obtained by the calcination of green vitriol. The use of chalk as a filling material is now rare. Zinc oxide is employed chiefly in the compositions of matches containing phosphorus sesquisulphide, red phosphorus and the like.

The above substances can all be obtained in the requisite degree of purity.

D. BINDING SUBSTANCES

1. Glue [2]

I. THE COMPOSITION AND MANUFACTURE OF GLUE

Boiling water extracts from certain portions of vertebrate animals a material known as glue. These portions are the connective tissues and the intercellular substance of the sinews, ligaments, bones and dentine. A genuine glue contains mainly the complex nitrogenous organic substance gelatin. A number of other substances are often called glues: for example, starch glues, casein glue, marine glue, and various mineral and vegetable adhesives. The nature of glue is to some extent determined by the class of tissue from which it is made. The various tissues from which glue is obtained can be briefly classified as follows: ossein in bones and skin, chondrigen of cartilage and isinglass from the bladders of fish. These three classes are included under the general heading of *Collagens*.

The British Standard Method for testing glues and gelatines [3] falls under two headings: (*a*) physical (mainly degree of hydrolysis), and (*b*) chemical, *i.e.* tests for purity. The tests include those for moisture, jelly strength,[4] viscosity, melting point, foam formation, water absorption, the solubility of the partly swollen sheet, keeping quality, *p*H, grease, ash, sulphur dioxide, chlorides, the colour of the jelly and of the solution, clarity, arsenic and heavy metals.

For commercial glues the tissues classified as the collagens supply the only practical raw material. The glues from this source may be classified as follows:—

[1] B.P. 436553 (1935).

[2] A review of the composition and testing of glue is given by Lageløz, *Rev. chim. ind.*, 1935, 182.

[3] *B.S.* 757, 1937 (price 3s. 6d.).

[4] Bloom gelometer, *Ind. Eng. Chem.* (*Anal.*), 1930, **2**, 348.

1. *Glutin* is the main constituent of commercial glue[1]; it has the approximate composition :—

Carbon	50·0	per cent.
Hydrogen	6·6	,,
Nitrogen	17·8	,,
Sulphur	0·25	,,
Oxygen (by diff.)	25·2	,,
Ash	0·2	,,

It swells in cold water without dissolving. On heating it changes to a liquid and on cooling again gelatinizes. It is soluble in acids and alkalis at laboratory temperature. On continued boiling with water, glutin loses its solidifying property (*i.e.* its property of gelatinizing on cooling). It is not precipitated by acetic acid, potassium ferrocyanide or nitric acid, and in this way differs from the true albuminoids. Most varieties of tannic acid throw it out of solution.

2. *Chondrin* is somewhat similar to glutin, but is more horny in structure and its adhesive power is less. It is obtained by boiling cartilage with water; the resulting opalescent liquid gelatinizes on cooling. It can be precipitated by dilute mineral acids but redissolves in excess. It is sometimes regarded as a mixture of glutin with mucin. Mucin is generally regarded as a mixture of complex organic substances which are generally removed during the liming process. They have practically no adhesive properties, and if present in glutin to any appreciable extent they give rise to foaming when the solution is warmed.

Commercial gelatin glues are divided into various classes, according to the raw products from which they are made, as follows :—

Skin Glue. For the manufacture of this glue, waste materials from the slaughter-house are used. The inner skins contain a large amount of connective tissue which, on extraction with boiling water, yields glue. The first process consists of a treatment with lime or sodium sulphate in open, shallow pits for several days, with repeated agitation. The insoluble material is then washed and scraped to remove hairs and flesh. The cleaned material is next boiled with water in open vessels and the resulting solution (which contains the glue) is filtered and concentrated *in vacuo* at approximately 60°. The resulting dark viscous solution is decolorised by charcoal and sulphur dioxide and the hot filtered solution allowed to settle.

Leather scrap may also be utilized for glue manufacture by digestion with an aqueous solution containing 5 per cent. of sodium hydroxide on the weight of the dry leather scrap. The mixture is boiled until the glue-like substances are liberated, drained and filtered.[2]

[1] According to Gerngross, *Z. angew. Chem.*, 1929, **42**, 968, the glutin content is the true criterion of quality.

[2] U.S. Pat. 1283474/1918.

The solution is then decolorised, if necessary, and concentrated. A clear glue can also be obtained by agitation with porous vegetable material of open texture, possessing approximately the same cellular structure as that of the material from which the glue is made.[1] Kieselguhr may also be added and the filtered decolorised solution further concentrated.

Bone Glue. This type of adhesive is obtained from bones of various types. The fat is first removed by a restricted steaming in a digester or by solvent naphtha or petroleum. To extract the glue the bones are heated under pressure with steam in special autoclaves. The calcium phosphate may be first removed by acids and the residue steam treated. The solution after clarification is concentrated *in vacuo*.

Fish Glue. Various types of fish offal are used and the treatment is somewhat similar. Glues of this type are generally deodorised to some extent by the use of sodium phosphate or otherwise.

The addition of potassium dichromate to the glue is stated to make the match composition gradually damp-proof owing to the oxidation of the glue.[2]

A water-soluble albumin has also been proposed as an ingredient in the mixture for match-heads and striking surfaces.[3] The binding agent containing a soluble albumin is rendered insoluble in water during drying of the composition.[4]

II. Properties and Examination of Glue

Glue is mainly used for its adhesive and binding properties. A good glue should be very hard and not readily brittle. When struck with a light hammer it should give a loud, sharp sound. It should be clear and transparent with a pale colour, with freedom from foreign particles. This latter property may give rise to mistakes, as the so-called benzine glues, although thin and pale-coloured, are, as a rule, inferior to true gelatins. When placed in cold water it should only swell and take up a large volume of water without dissolving; the water should have at most only a faint odour and should not show any appreciable cloudiness. On heating to 50° good skin glue should completely dissolve. Numerous methods are in use to test the quality of glue. Lipowitz estimates the bearing power of a gelatinized glue solution of definite concentration (generally 10 per cent.) at a definite temperature. The glue is placed in cylinders which are closed with a lid through which, in a guide tube, passes a stout wire, to the lower end of which is fixed a convex disc. On the other end is

[1] U.S. Pat. 1289053/1918.
[2] *Dept. Industries Bengal Bull.*, 1928, **23**.
[3] B.P. 314852/1929.
[4] See Lovern, *Byproducts of the Fishing Industry* (*Fish Glue.*)

fixed a balance pan. The convex surface rests on the top of the jelly and weights are added until the lower disc penetrates. The greater the weight added, the greater the consistency.

Liquid Glue can be obtained by treating 100 parts of glue with 140 parts of water and 16 parts of nitric acid ; it still retains the adhesive power of the glue used in its production, but does not gelatinize. This glue, and also liquid glue made with acetic acid, will not serve for the manufacture of match compositions.

Water Resistant Glue. The addition of formaldehyde polymerides or related compounds to animal glues produces a water resistant glue.[1]

Examination. A weighed quantity of dry glue is allowed to remain for twenty-four hours in cold water, then allowed to dry and weighed again. The nearer the final weight approaches to the original, the better is the sample.

The desirable properties in a glue vary with the purpose for which it is to be used ; the buyer often lays chief stress upon the binding power of the glue. As the determination of the binding power is difficult, Kissling devised the following simplified scheme for testing glue.

(1) Kissling's Scheme for Testing Glue

1. *Determination of Moisture.* A sample is removed from the slab of glue with the aid of a coarse wood rasp, 2 to 3 g., quickly weighed out on to a large watch-glass, and dried to constant weight in an air-oven at 110° to 115°. It is absolutely necessary to carry out the drying with finely powdered glue, for the moisture cannot be completely expelled at the above temperature from larger particles, and it is advisable to resort to a higher temperature. The moisture content of a good glue is generally between 10 to 20 per cent. A lower result indicates that the glue has been overheated in drying and the adhesive properties may be affected. Powdered glue loses very perceptibly in weight, if allowed to stand in the laboratory at the ordinary temperature for some time.

2. *Determination of Ash.* For the determination of the ash it is convenient to use the same sample of glue as was taken for the moisture determination. It is incinerated in a covered platinum or silica crucible, the full heat of a Bunsen burner being at once applied. The traces of mineral matter which are lost in this shortened method may be neglected without danger, since only great differences in the quantity of ash need be taken into account. The last particles of carbon, which are somewhat difficult to remove, are best burnt by repeatedly allowing to cool, moistening, and igniting the contents of the crucible.

[1] *Ind. Eng. Chem.*, 1925, 225.

3. *Qualitative Examination of the Ash.* The nature of the ash generally gives reliable indications as to whether the glue was derived from bone or from hide. The ash of bone glue melts at the temperature of the Bunsen burner, its aqueous solution generally reacts neutral, and its solution in nitric acid gives the reactions for phosphoric and hydrochloric acids. If the ash has been very strongly ignited, deposits of alkali chlorides are found on the inside of the crucible cover and sometimes on the edge of the crucible. The ash of skin or hide glue contains a large proportion of lime and remains therefore unmelted. It reacts strongly alkaline and is generally free from phosphates and chlorides. An unadulterated glue should have an ash content of approximately 2·5 per cent. or less.

4. *Determination of Alkalinity.* To 2 g. of glue, dissolved in 18 g. of water, is added 40 g. of 99 per cent. alcohol; after brisk agitation, the mixture is filtered and titrated with $N/10$ hydrochloric acid, phenolphthalein being employed as the indicator.

5. *Free Mineral Acid* is determined by titrating a 10 per cent. solution of the glue in water with aqueous sodium hydroxide solution, successive portions of the liquid being spotted on to neutral litmus paper. The quantity of alkali to be added each time before the spotting must correspond to 0·005 g. H_2SO_4. During the titration, the glue solutions are warmed to about 30°. Phenolphthalein may be used as indicator.

6. *Determination of the free and combined Volatile Acids.* 30 g. of the glue is covered with 80 g. of water in a round-bottomed flask and placed aside for a few hours to allow the glue to swell. An arrangement is then fitted up which permits of the removal of the volatile acids by steam distillation, the flask being conveniently placed in a vessel containing boiling water, in order to avoid the condensation of any considerable quantity of steam. As soon as the distillate no longer has an acid reaction, the distillation is stopped, and the quantity of acid is determined by titration. To liberate the combined volatile acids, the contents of the flask are next acidified with concentrated sulphuric acid, and distilled again in a similar manner. In some instances the distillate contains considerable quantities of sulphurous acid, so that it is advisable to distil into a known quantity of standard alkali. The sulphurous acid can be converted into sulphuric acid by the addition of bromine, and then determined gravimetrically. The acid content of a good glue is generally less than 0·2 per cent.

7. *Determination of the Drying Properties.* The solution of glue, freed from volatile acids, is diluted with water to a weight of 150 g. and again heated to the temperature of boiling water with an upright tube to prevent loss by evaporation. 10 ml. is then withdrawn by a pipette on to the middle of a watch-glass of about 10 cm. diameter, in

such a way that no glue is present on the glass outside the circular disc of jelly, the centre of which must coincide with that of the glass. The watch-glass is placed in a horizontal position before the addition of the glue; it should be allowed to remain in a place as free as possible from dust and draughts, and where the temperature is not liable to fluctuate greatly. The alterations of the glue are then observed for a few days. According to the drying properties of the glue, the jelly dries more or less quickly from the edge to the centre, and from the size of the patch which still remains soft after a certain time, a fairly reliable conclusion can be drawn as to the drying properties of the sample. As the process of drying is greatly influenced by the degree of moisture and temperature of the air, and as it is very difficult to keep these constant, it is advisable always to carry out comparative determinations. It is, therefore, advantageous to compare the glue under examination with two samples which have been previously tested, one of good, and the other of inferior drying properties, the three being treated identically, as above.

8. *Determination of Foreign Matter.* Kissling recommends only an approximate quantitative determination of the total quantity of those substances which are deposited when the glue solution is sufficiently diluted. The separation of these substances by filtration is troublesome and slow, even after partial separation by decantation, so Kissling makes approximate determinations of the volume of the solid deposit, since the estimation is only comparative. The glue solution referred to in (7)—that is to say, 150 ml. less 10 ml.—is diluted with hot water, allowed to cool, introduced into a cylinder of 1000 ml. capacity, graduated in ml., filled up to the mark, mixed and allowed to stand. The volume of the solid deposit, after twenty-four hours, forms a measure of the quantity of insoluble "foreign matter" in the glue. This is generally very small, but in some cases considerable. Such substances decrease the binding quality of the glue when they consist to a great extent of organic matter.

9. *The Odour.* This feature is of especial importance, as it gives indications concerning the durability of glue, and its tendency to decompose. The smell of glue varies greatly according to the quality. Usually, hide glues are in this respect superior to bone glue. With some kinds of glue, the smell of the cold slabs is very slight, whereas the hot jellies have a very unpleasant smell. In such cases the glued surface, after drying, has a much more unpleasant smell than the cold slab. In his published results, Kissling therefore gives indications of the smell, both of the dry glue and of the hot jelly. Obviously, it is only possible to judge the odour accurately after carrying out a long series of investigations of glues.

In general a satisfactory agreement has been found between the

results of practical experience and those of Kissling's tests. The amount of acidity determines the suitability of a glue for some purposes. The quantitative estimations of water, ash and fat (see p. 599) are generally of minor importance. Hide glues show a superiority over bone glues, but it must be emphasized that the manufacture of bone glue has undergone such improvements that its relative value in comparison with hide glue has greatly increased. The best bone glues now compare approximately with medium skin glues.

In a subsequent publication, Kissling[1] emphasizes the fact that all forms of apparatus devised for the purpose of directly measuring the binding power,[2] the first requirement in the testing of glues, fail to give even approximately concordant results under identical conditions of experiment. This is, at all events, his experience with apparatus devised by himself for this purpose (*loc. cit.*), and for this reason he prefers the determination of the drying properties of glue. In a later paper[3] he strongly advocates, and describes an apparatus for, ascertaining the melting point of the glue jellies.

The main conclusions from a paper by E. G. Clayton,[4] on the technical examination of glue, based on investigations of a number of samples of British and foreign origin, are as follow :—Colour is of limited value as an indication of quality, and too much importance is often attached to it. Some dark-tinted glues may be better in quality than comparatively pale samples. Air bubbles should be few, or better, absent. The odour of samples should be inoffensive. Good glue should not deteriorate quickly on exposure. Physical tests usually lead to more definite conclusions than analyses, but some of the chemical data are very useful. Perhaps the best *single* chemical test is Stelling's—the determination of non-gelatinizing matters by precipitating with alcohol, filtering, evaporating a fractional part of the filtrate, and weighing the dried residue. A high result appears to be a *primâ facie* indication that the glue, at all events, is below the best standard of quality. Hygrometric, immersion, jelly-drying, viscosity, and other tests are described in the paper. The viscosity test and Kissling's jelly-consistency test are favourably reviewed, and the hygrometric test (rate of absorption of moisture from air saturated with aqueous vapour) is stated to give useful indications. Finally, it is remarked that whilst it would be rash to form a judgment on glue from a single test, the evidence afforded by a number of tests may be decisive.

The hydrogen ion concentration of a glue may often be an important determination as giving an opinion of the value of such product,

[1] *Chem. Zeit.*, 1889, 13, 1667.
[2] An apparatus for this purpose has been described by Horn, *Chem. Ind.*, 1887, 1, 297.
[3] *Chem. Zeit.*, 1900, 24, 567 ; 1901, 25, 264. [4] *J. Soc. Chem. Ind.*, 1902, 21, 670.

according to Bogue.[1] If the *p*H value is 4·7 the viscosity will be low and the product nearly insoluble. On either side of this point the properties change considerably, attaining their maximum on the acid side at *p*H 3·5 and on the alkaline side at *p*H 9·0. The measurements may be made by electrometric or colorimetric methods. The effect of *p*H on the elasticity of gelatin jellies has been studied by Sheppard, Sweet and Benedict.[2] If glue is brought to the isoelectric point (near *p*H = 5·0) by the addition of acid or alkali, the matter in colloidal suspension is flocculated and easily removed.[3]

(2) Methods for the Determination of Fat in Glue

W. Fahrion[4] recommends the following process:—10 g. of broken glue is warmed on a gently boiling water-bath with 40 ml. of 8 per cent. alcoholic sodium hydroxide in a porcelain dish, with constant stirring, until the alcohol is completely driven off. If complete solution does not occur, the residue is taken up with alcohol and again evaporated to dryness. The transformation product of the glutin, as also the sodium salts of the fatty and hydroxy-fatty acids dissolve readily; any residue which is found, consists of inorganic matter, and dissolves on subsequent acidification with hydrochloric acid. The acidified solution is heated for about half an hour almost to boiling, then washed into a separating funnel, and after cooling, well shaken with ether and allowed to stand for a considerable time, best over night. The acid aqueous liquid is drawn off, and the ethereal solution which contains the fatty acids and the liquid hydroxy-fatty acids is poured off at the top. The solid hydroxy-acids which remain behind in the funnel are dissolved in warm alcohol, the ethereal and alcoholic solutions combined and evaporated, the residue weighed, ignited, and again weighed and the difference taken as the fat. The results obtained in this way agree satisfactorily among themselves, but are always too low, for two reasons. Firstly, any glycerin present in the glue fat is not determined with the fat, and secondly, the hydroxy-acids are not quite insoluble in acidified water. The error which results in this way is, however, very small, and the figures are throughout higher than those obtained by Kissling's method. For instance, the quantity found for a brown joiner's glue by Kissling's method was 0·21 per cent., by Fahrion's method, 0·51 per cent., and in an almost white skin glue, by Kissling's method, 0·13, and by Fahrion's method, 0·40 per cent. of fat.

According to the method of Kissling, only that part of the fat which is soluble in petroleum ether, is determined. The fat contained

[1] *Ind. Eng. Chem.*, 1922, **14**, 439.
[2] *J. Amer. Chem. Soc.*, 1922, **44**, 1857.
[3] U.S.P. 1895446.
[4] *Chem. Zeit.*, 1899, **23**, 452.

in glue is, however, partly oxidized, and oxidized fats are in some cases insoluble in petroleum ether.[1] The raw materials for the manufacture of glue, namely, skin and bones, already contain oxidized fat. Further, the glue decoction is repeatedly heated in presence of air, and finally the drying of the glue brings it into such intimate contact with the air that the oxidation of the fat probably proceeds further. Indeed, Fahrion found in a skin glue only 0·08 per cent. of fatty acids as compared with 0·31 per cent. of oxidized fatty acids.[2]

(3) Differentiation of Animal and Vegetable Glue[3]

The distinction between animal glue and dextrin glue, or between gum and mixtures of gum or dextrin with animal glue, is based upon the well-known reaction towards Fehling's solution, which is reduced in presence of dextrin on boiling. So-called plant glue (albumin glue, gum), which is prepared from wheat gluten and is used for gumming and cloth dressing, is very similar to animal glue in its physical and chemical properties, particularly to inferior bone glue. Its aqueous solution gives, like animal glue, a voluminous gelatinous or cheesy coagulum with tannin solution; with a little aluminium sulphate solution it gives no precipitate, or at the most only a slight separation, but with larger quantities of aluminium sulphate it yields a greater amount of a flocculent or cheesy precipitate, whilst with lead acetate it undergoes no change. In general, vegetable glue swells and dissolves with more difficulty in water than animal glue, and the solution gelatinizes less readily on cooling. A trustworthy method for distinguishing between the two cannot, however, be based upon this property. Both animal and vegetable glue give flocculent precipitates with concentrated sodium sulphate, which, however, redissolve on warming. If the solution be boiled for some time and treated with lead acetate, animal glue gives a white or pale grey precipitate, while vegetable glue, containing, as it does, larger quantities of sulphur, generally gives a black precipitate, less frequently a grey one. An aqueous solution of vegetable glue gives on warming with Millon's reagent a violet-red coloration, like all albuminoid substances; in many cases, however, inferior animal glue behaves in the same way.

A simple and trustworthy method for distinguishing between animal and vegetable glue is the following:—The sample of glue (about 1 g.) is dissolved in water (10 ml.) by warming, a drop of sodium hydroxide

[1] Recent development in low temperature drying and grease extraction by solvents of bones for glue and gelatin manufacture is described in *Kunstdünger u. Leim.*, 1932, **29**, 398.

[2] Cf. *Chemie und Technologie der Leim- und Gelatin-fabrication*, Gerngross and Goebel (Dresden, 1933).

[3] A review of the history, chemistry, manufacture, testing and grading of animal and fish glues is given in *Paper Industry*, 1935, 410.

solution being added if necessary. A few grams of common salt or magnesium sulphate are then added, and the whole shaken. The solution of animal glue remains clear, whilst vegetable glue separates almost completely as a voluminous or gelatinous precipitate. Mixtures of animal and vegetable glue can be readily recognized in this way.

(4) Physical Tests

The physical examination of glue, especially viscosity, rate of drying, gelatinization point, joint strength, elasticity, etc., are important and are often determining factors in judging the value of a glue.[1]

(*a*) **Viscosity.** — According to the investigations of Fels,[2] the consistency of glue is closely related to the quality or binding power. Neither the quantity of water taken up, nor the examination of the mode of fracture gives trustworthy indications of the practical value of a glue, but the viscosity of the solution is a better index of quality. The reason of this is evident; glues which have been prepared under the influence of lime or acids give rise, under certain conditions, to a less consistent jelly than a properly manufactured product, namely, when the lime or acid has not been sufficiently carefully removed from the glue. The decomposition products which result in presence of lime or acids, especially on boiling or steaming the glue-producing substance, as also those which result when too high a steam pressure has been used, diminish the consistency of the jelly, as does also a badly regulated concentration of the glue solution, or even an incipient organic decomposition of this solution.

The method of determining the consistency of the jelly obtained from a glue is carried out as follows :—

1. *Determination of Moisture.* The sample is broken up, 1 to 2 g. of powdered glue obtained from the fragments, with the help of a file, rasp, or knife, and this quantity is dried for two hours at 100°.

2. *Preparation of the Test Jelly.* About 100 g. of the glue under examination (viz. the broken pieces from which the fine powder was filed) is placed in a beaker of 500 ml. capacity, and about 400 ml. of cold water added; after twenty-four hours the swollen glue is dissolved by heating on a water-bath. The dilution is carried out in such a way that a 15 per cent. jelly results, calculated on the anhydrous glue.

Clark and Du Bois [3] describe a physical test for glues. It consists in determining the weakest solution of the glue which gives a solid jelly at 10°. If a 6 per cent. solution of the substance is liquid and a 7 per cent. solution is solid, the jelly is said to have a comparative

[1] *Cf.* Jennings, *Chem. Trade J.*, 1933, **92**, 105. The National Association of Glue Manufacturers (U.S.A.) has specified standard methods of sampling, preparation and testing of samples by viscosity, jelly strength, etc. See *Ind. Eng. Chem.* (*Anal.*), 1930, **2**, 348, and also *B.S.* 647, 1938.

[2] *Chem. Zeit.*, 1901, **25**, 23.

[3] *Ind. Eng. Chem.*, 1918, **10**, 707.

jelly value of 7 per cent. The comparative strengths of glue jellies can be found by determining the ease with which swollen particles of glue melt and slide when placed on a sloped brass plate. The lower end of the plate is dipped into water and kept at 40°. The better glues retain their grip on the plate for the longer period.

3. *Determination of the Viscosity.* Engler's viscosimeter is especially good for this purpose. First, the viscosity of water at 30° is determined, and used as a unit for the subsequent glue tests. The same determination is then carried out with the 15 per cent. solution of glue, also at 30°. The time of flow of the latter divided by that of water gives a number which expresses the consistency of the glue.[1]

Some results obtained by this method of examination are given in the following table. Sample No. 2 was quite slimy after a few hours and sank together to a lump, whereas No. 5 preserved its original form and gave up no particles of jelly, even when scraped with the finger. Further, it was found that Nos. 3 and 5 became a solid jelly after twelve hours, whereas No. 2 was still a thin jelly, and underwent no alteration even after a further period of twenty-four hours :—

Description of sample.	Substance used, in grams.	Moisture content per cent.	Corresponding quantity of anhydrous substance.	Dissolved to ml.	Time of outflow of 500 ml. in seconds. (Time of outflow of water at 30° = 90 seconds.)	Viscosity.
1. Light yellow, transparent thick slabs .	95·0	16·3	79·6	530	149	1·65
2. Brown glues, transparent	95·0	14·0	81·7	544	125	1·38
3. Wine yellow, transparent slabs . .	88·7	15·4	75·1	500	171	1·90
4. Light yellow slabs, breaking into small pieces . . .	100·0	18·2	81·8	545	150	1·66
5. Semi-opaque glue .	100·0	15·2	84·8	565	199	2·21

In the MacMichael viscosimeter[2] a plunger of standard size is used, suspended by a torsion wire above the instrument. The glue is placed in a cup which is rotated at a constant speed on a motor-driven platform. The viscosity determines the twist on the wire which is measured by a disc attached to the spindle.

The viscosity of gelatin and glue is affected by the acidity of the material, by the age of the solution, and by other factors. A method of testing glues suggested by Lenk[3] consists in measuring the time of gelatinization in minutes at pH 7·0—7·5. He proposes the

[1] For practical details in the carrying out of viscosity, see Reilly and Rae, *Physico-Chemical Methods*, 1940; and *Physico-Chemical Practical Exercises*. London, 1934.

[2] *Ind. Eng. Chem.*, 1916, 916. [3] *Biochem. Z.*, 1926, 177, 634.

formula $y = -0{\cdot}55\ x + 1{\cdot}8$, where x = log. of gelatinization figure in minutes and y=viscosity.

Goebel[1] determines the viscosity of hide and leather glues in 17 per cent. solution at 40°, and of bone glue at 30°. He uses either an Engler or Vogel-Ossay instrument and determines the concentration by means of a Suhr glue hydrometer calibrated in percentages. Apparatus for the modulus of elasticity of glue and gelatin is described by Sauer[2] and by Goebel.[3]

(*b*) **Melting Point of the Glue Jelly.**—Kissling considers[4] that such chemical methods as precipitation with tannin, or estimation, of the percentage of nitrogen, are unsuitable for adjudging the value of a glue. In a paper by this author[5] on the testing of plates of glue, a method for the determination of the melting point of the glue jellies and a convenient apparatus for the purpose, are described. The apparatus and method have given good results in the practical manufacture of glue.

A bath of copper or other metal partially filled with water at 50° serves as the source of heat. The bath should be filled to a mark placed at two-thirds of its height, and the temperature is kept constant during the experiment. The bath is fitted with a removable cover consisting of a vessel, the bottom of which is covered with a sheet of asbestos upon which rests a ring-shaped receiver. In this a thermometer and the small cylinders containing the glues are placed. The upper vessel is covered with a glass plate. It is advisable to cover the outside of the vessel with asbestos. The method of working is as follows:—15 g. of the glue samples to be tested and 30 g. of distilled water are introduced into small flasks, each fitted with a straight tube about 1 metre long. The flasks are allowed to stand over night and then heated in boiling water until the glue has dissolved completely, solution being accelerated by shaking the flasks with a circular motion. The flasks containing the lukewarm glue solutions are then fitted into the glass cylinders, which are made exactly to a specified size and are provided with ring-shaped marks; the cylinders are closed with corks and placed in a holder, the base of which consists of a brass sieve, over which two intermediate discs are fixed, each containing seven holes. The cylinder containing the thermometer is placed in the middle, and contains a concentrated solution (1 : 1) of the best hide glue. The receiver thus filled is allowed to stand for an hour in water, the temperature of which is kept at 15°. After the thermometer vessel and test cylinders have been thus brought to the same temperature, they are quickly brought into the thermostat, which has been

[1] *Kunstdünger u. Leim.*, 1932, 3, 60, 97, 142, 358.
[2] *Chem. Fabrik.*, 1933, 293.
[3] *Kolloid Z.*, 1933, 62, 54.
[4] *Z. angew. Chem.*, 1903, 16, 398.
[5] *Chem. Zeit.*, 1900, 24, 567; 1901, 25, 264.

fitted up as above, and the melting point of the glue jelly determined. The melting point is the temperature at which the horizontal surface of the jelly begins to become uneven. The higher the melting point, the higher is the content of gelatinizing substance. In addition, this simple method gives direct indications as to the degree of firmness of the glue jelly, which is of importance in certain cases, as, for instance, in glueing casks.[1]

As regards the testing of plates of glue, the question whether a glue is good or bad, useful or useless, cannot be answered in a general way unless it is so inferior in quality that it can be discarded at once as worthless. In the great majority of instances the purpose for which it is to be used must be known ; hence a glue can only be designated as unsuitable for a specific purpose.

So far as the binding properties are concerned, numerous experiments have shown that even inferior bone glues are satisfactory, and hide glue of high quality scarcely shows any superiority in this respect. If, therefore, only the binding properties have to be taken into consideration, there is no object in using the more expensive hide glues. This does not hold good for the degree of firmness. Experiment has shown that hide glues are in general superior to bone glues in this respect, although some samples of the latter yield moderately firm jellies. As is well known, the method of manufacture plays an important part in reference to this property ; the larger the quantity of glutin that is converted to glutose during the manufacture, the less firmness does the jelly possess, and in this respect the manufacture of bone glue has undergone great improvements.

Considerable weight is attached by some writers to the " Foam-test." [2] Foam is due to over-boiling, which causes peptonization. A good glue, it is stated, should yield a minimum foam, when the solution is shaken, coupled with a maximum jelly consistency.

(*c*) **The Binding Power.**—1. *Setterberg's*[3] *Method.* This author soaks strips of unglued paper in a glue solution of known concentration, removes the excess of glue by pressing between blotting paper, and when dry, estimates the binding power of the glue by subjecting the strips to tearing tests in a paper-testing machine.

2. The adhesive power of glue can be determined by the method of Rudeloff.[4] A standard aqueous solution of the glue is applied to two wooden surfaces of definite areas. The surfaces are previously cleaned and dried at 40°. Two wooden glued surfaces are placed in contact, and the films allowed to make contact at a pressure greater

[1] *Cf.* L. E. Campbell, " Calibration of Jelly Testers," *Chem. and Ind.*, 1937, **57**, 413.

[2] *Cf.* S. R. Trotman and J. E. Hackford, " Conditions affecting the Foaming and Consistency of Glues," *J. Soc. Chem. Ind.*, 1906, **25**, 1905.

[3] Post, *Chem. techn. Anal.*, vol. ii., p. 857.

[4] *Mitt. K. Materialprüf.*, 1918, **36**, 2.

than 0·84 kgm. per sq. cm. The force required to separate the glued surfaces after a definite time is then measured.

3. *Weidenbusch's test for Binding Power.*[1] This test gives reliable results. Exactly equal prismatic rods of plaster of paris, 9·2 cm. long, with the side of the transverse section 4 mm., and having a weight of 1·7 g., are dipped in a glue solution for five minutes, then taken out, and allowed to dry. They are then placed on an iron ring, which is fastened in a horizontal position, so as to form the diameter ; a dish is hung to the centre of the rod, into which weights are placed until the rod breaks. The better the glue, the greater the weight required to break the rod. By experiment it has been found that the relative adhesive power of skin glue to that of bone glue, is as 1·5 : 1 ; and, further, that glue made from calves' heads is better than any other class of glue. The following table bears out these facts :—

Class of glue.	Breaking strain.	Appearance of fractu
	Grams.	
Glue from crushed bones . . .	291·5	Even, four-sided.
Russian glue from Bohemia . . .	304·2	Even, fine-grained.
Saybusch glue, Lyon class . . .	351·2	Slightly uneven.
Cologne glue from A. Michl, Rehberg .	434·2	Uneven
Glue from calves' heads	483·7	,,
Plaster of paris rod before dipping in glue	103·2	Fairly even, fine grained.

Measurement of X-ray interference rings and X-ray analysis may aid in deciding the value of gelatins.[2]

Evaluation of a Glue from Viscosity Tests. The chemical analysis of a glue generally does not greatly help in its evaluation. The examination of moisture, ash and water adsorption give some information regarding the nature of the glue, but other tests are necessary, particularly those of a physical nature. The jelly consistency at low temperature or the viscosity at high temperature give useful comparative figures. Bogue [3] recommends the measure of the viscosity of an 18 per cent. solution at 35° by means of the MacMichael viscosimeter as an indirect test for the differentiation of glues and gelatins. It is recommended as a basis for the primary evaluation of these products. Tests of jelly consistency and viscosity at 60° are recommended for secondary evaluation.

For the rapid determination of the quantity of glue or gelatin in dilute liquors for the control of manufacturing processes physical methods are essential. Measurements of refractive index have been found very suitable.[4]

[1] *Cf.* Hanausek, *Lueger's Lexicon der ges. Technik.*, vol. vi., p. 136.
[2] *Collegium*, 1931, 67.
[3] *Ind. Eng. Chem.*, 1922, **10**, 434.
[4] Kane and Watson, *J. Soc. Chem. Ind.*, 1929, **48**, 44, 325 T.

Frei [1] used the Pulfrich refractometer with a single cell. Walpole [2] and Hart [3] used the Zeiss immersion refractometer. According to Kane and Watson, in order to obtain the full accuracy of which the Pulfrich refractometer is capable, it is necessary to know the compensation very closely. They overcame this difficulty by working with a double cell, one compartment being filled with distilled water and the other with the solution under examination. If this be done, provided sufficient time is allowed for the two liquids to reach the same temperature, it is only necessary to read the difference in refractive index on the micrometer and the temperature need not be measured at all. The method has the additional advantage that, owing to the position of the edge of the line being to a slight extent a matter of personal judgment, more accurate settings are possible when made on two lines in quick succession than when a considerable interval elapses between the readings.

The following results illustrate the accuracy of the method as worked out by Kane and Watson.[4] Kahlbaum's "Gold Label" gelatin was employed with a water content of 17·5 per cent., and ash 1·8 per cent. Solutions were made at 60°, filtered, and the gelatin determined by evaporation to dryness and heating at 105° for 15 hours.[5] More dilute solutions were prepared from the original by adding weighed quantities of water. The difference between the refractive index of the solution and that of distilled water was then read on the micrometer of the refractometer. Consecutive readings were found to differ by not more than 6 secs. The table below gives the concentration of the

Refractive Index of Gelatin Solutions at 21° and 29°.

G. gelatin per 100 g. water.	G. gelatin per 100 ml.	Difference in micrometer readings.	$\delta n_D \times 10^6$	$\delta n_D \times 10^5$/g. weight.	$\delta n_D \times 10^6$/g. volume.
21°					
0·122	0·122	2·80	22	180·0	180·0
0·202	0·201	4·65	37	183·0	184·0
0·320	0.318	7·30	58	181·0	182·0
0·526	0·524	12·15	96	182·0	183·0
0·710	0·705	16·25	130	183·0	184·0
0·879	0·872	19·95	159	181·0	182·0
1·330	1·316	30·10	240	180·0	182·0
1·784	1·754	40·40	323	181·0	184·0
29°					
0·780	0·772	18·15	143	183·0	185·0
1·130	1·116	26·10	207	183·0	185·5
1.592	1·566	36·60	291	183·0	186·0
2·406	2·356	54·95	439	182·5	186·3
3·215	3·137	72·85	584	181·7	186·2

[1] *Kolloid Z.*, 1910, **6**, 192. [2] *Ibid.*, 1913, **13**, 241. [3] *Ind. Eng. Chem.*, 1928, **20**, 870.
[4] *J. Soc. Chem. Ind.*, 1929, **48**, 44, 325 T.
[5] *Cf.* Sauer and Dillenius, *Z. angew. Chem.*, 1929, **42**, 552.

solutions, the difference in micrometer readings, the change in refractive index, which is not quite a linear function of the angular difference, and the change in refractive index per gram of gelatin for different concentrations. All measurements were made at room temperature, the first series during cold weather in the neighbourhood of 21° and the second series in hot weather at approximately 29°.

The concentration of gelatin has been given both in grams per 100 g. of water and grams per 100 ml., the latter being calculated by Kane and Watson by means of Davis and Oakes' formula,[1] $D_g = D_w + 0{\cdot}0029x$, for the density of a solution containing x per cent. of gelatin. It will be seen that the relation between change in refractive index and concentration is very nearly linear whichever method of expressing the latter quantity is adopted, the variation being slightly less for volume concentration.

For recent development, both scientific and technical, in the glue industry see Simon, *Kolloid Z.*, 1938, **84**, 102.

(5) Commercial Varieties of Glue [2]

Joiners' Glue is either skin glue or bone glue, or a mixture of the two.[3] *Cologne Glue* is the best and purest skin glue, and is very much in request on account of its high adhesive power. *Gilders' size* is Cologne glue in thin leaves bleached by chlorine. *Patent Glue* is a pure, dark-brown bone glue in thick tablets, without net-markings; it swells greatly in water, and serves for mouldings, buttons, and the like. *Fining Glue* is manufactured from bones in the form of thick, pale-tinted plates, and is used instead of isinglass for the fining of wine and beer. *Mouth Glue* is a better quality of bone glue, scented with lemon essence and sweetened with sugar. *Russian Glue* is a dingy white or brownish-white variety of Cologne glue, rendered opaque by the addition of white lead, zinc white, permanent white, or chalk. An improvement in adhesiveness is not aimed at by the additions.

Glazing and *parchment size* are valuable kinds of pure skin glue, resembling gelatin; parchment size is put on the market in jelly form, packed in small jars, usually with an addition of alum. *Flemish Glue* consists of thin, yellow leaves, shrunken in both directions, and is used for the production of glue colours and as a glazing material. *Paris*

[1] *J. Amer. Chem. Soc.*, 1922, **44**, 464.

[2] The National Association of Glue Manufacturers Inc. (55 West 42nd Street, New York U.S.A.) have published various recommendations (revised to 1930) for the testing of various types of glues. The methods for viscosity determination are outlined in *Ind. Eng. Chem.*, 1924, **16**, 310.

[3] *B.S.* 745, 1937, gives the latest specification for joiner's glue.

Glue and *Hatters' Glue*[1] are poor, dark brown, opaque, almost always offensively smelling, soft varieties, used in hat-making because of their considerable hygroscopicity.

Liquid Glue. 38 parts of glue are dissolved in 100 parts of acetic acid; the resulting product remains in the fluid state. A preparation made with nitric acid is known as *Steam Glue*, also as *Russian light* and *dark Steam Glue*. *Glycerin Glue* is obtained by dissolving glue in warm glycerin; small additions of glycerin to steeped glue impart elasticity to the jelly, making it caoutchouc-like and suitable for hectograph compositions. *Chrome Glue* is either a mixture of glue with potassium or ammonium dichromate, or of glue with chrome alum. After drying, the former mixtures are insoluble in water. They are used for cementing glass, porcelain, and iron, for finishing and waterproofing materials, and for photographic purposes.

2. Gums

Three sorts of gums are used in the manufacture of matches—gum arabic, gum senegal and gum tragacanth.

(a) *Gum Arabic* forms irregular, brilliant, transparent, brittle pieces of a white to yellow or brown colour and varying from the size of a lentil to that of a walnut. The pieces are mostly filled with internal cracks, and are also cracked on the surface, which renders them easy to break and to powder. They do not become damp in the air, show a brilliant conchoidal fracture, and give with cold water an almost clear, viscous, slimy, slightly opalescent solution, which can to some extent be drawn out into threads, but which is neither tough nor gelatinous. The solution reacts faintly acid and is very adhesive. Gum arabic breaks up and dissolves easily in the mouth, and has an insipid and slimy taste. The solutions are thick flowing and have a good adhesiveness.

On account of its high price, it is frequently adulterated, mostly with insoluble cherry-gum, dextrin, etc., and is sometimes bleached with sulphurous acid to make it appear of better quality for certain purposes. This renders it unsuitable for the manufacture of matches. Since the conditions of export from the Sudan have become unfavourable, gum arabic is adulterated with gum senegal; indeed, according to Liebermann,[2] the latter is often sold as gum arabic. The solution, which is generally slightly acid, is heterogeneous.

(b) *Gum Senegal* forms round fragments which are larger and more transparent than gum arabic, and have fewer cracks penetrating to their interior. The pieces frequently contain large air bubbles,

[1] *Cf.* Valenta, E., *Die Klebe- und Verdickungsmittel*, *Kassel*, 1884, p. 123.
[2] *Chem. Zeit.*, 1890, 14, 665.

formed like tears, their surface is rough and not brilliant, they vary in colour from almost white to reddish-yellow, and their fracture is coarsely conchoidal and very brilliant. It is more difficult to dissolve than gum arabic, the solution is more gelatinous and less adhesive. It mixes well with organic acids and with alkalis.

According to Liebermann,[1] gum senegal forms either colourless pale yellow, or superficially white pieces, resembling etched glass in appearance, which, however, are bright and transparent internally. The pieces are generally long, straight, coiled, or cylindrical with concentric rings. Roundish fragments of various sizes are, however, also met with, which have the appearance as if a large drop had become incrusted with smaller pieces after solidifying.

If the gum under examination has not been artificially powdered (by pounding), it is sufficient to observe these external properties to distinguish gum arabic from gum senegal. Other gums can also be detected, in this case, according to Liebermann, by the deviation of their appearance from the above.

Gum senegal is said to be distinguished from gum arabic, apart from the above method, by its property of gradually becoming moist on exposure to the air, as also by the fact that it gives only a slight turbidity with mercurous nitrate, and is very markedly thickened by borax. According to Liebermann and Kramsky,[2] however, the assertion that gum senegal is more hygroscopic than gum arabic is incorrect. The percentage of water in each kind of gum was determined at 105°, and the dried substance allowed to stand for twenty-four hours in moist air and again weighed. Gum arabic proved to be slightly the more hygroscopic of the two, as shown by the following data :—

	Gum senegal.	Gum arabic.
Water	13·39 g.	14·56 g.
Water absorbed in twenty-four hours by the dried samples	6·15 g.	6·34 g.

Gum senegal coagulates with a number of chemical reagents, for which reason match-heads prepared with this gum are often not very cohesive.

(c) *Gum Tragacanth* comes into commerce in many different varieties. It is tasteless and inodorous, transparent, horny and tough, so that it is difficult to powder. Only a small part actually dissolves in water ; for the most part, it swells up, forming a mucilage, which is not sticky, but nevertheless is highly adhesive, and can be mixed with water if in sufficient quantity. It is therefore added to the igniting composition for matches (especially safety-matches) in small quantities, firstly, in order to keep the heavier particles in

[1] *Loc. cit.* [2] *Chem. Zeit.*, 1890, 14, 665.

suspension, and secondly, to impart greater hardness to the glue or gum-mass after drying, and thus to protect it from climatic influences. In the preparation of mucilage from gum tragacanth a short boiling gives a more viscous solution. Prolonged boiling decreases the viscosity.

It is advisable to dry the tragacanth very thoroughly, as this renders it more brittle, and facilitates the grinding. It should be coarsely ground, because it then dissolves more readily, or rather, swells more uniformly and quickly.

Powdered tragacanth gives a turbid mucilage with 30 parts of water, and this is coloured yellow by sodium hydroxide, when the mixture is heated for a short time on a water bath. At ordinary temperatures, both powdered tragacanth and the mucilage prepared from it remain completely colourless for hours, on addition of sodium hydroxide. (Reuter.[1]) The better the quality of the gum the more readily is it precipitated by solutions of sodium hydroxide or by borax.

A cheap substitute for tragacanth, discovered by Boschau, is a mixture of 20 parts of starch, 6 parts of glue, and 2 parts of glycerin, boiled in water, which is stated to be quite as efficient as tragacanth in its action. Semi-soluble gums and various mucilages such as that from Carraghin moss or Iceland moss have practically no application in the match industry, as they are difficult to prepare without suspension and they easily ferment.

There is no direct chemical method of determining the values of gums. The following, however, are useful tests and give some information regarding the gums: (*a*) ash content, (*b*) acidity, (*c*) moisture content, (*d*) keeping property of the gum. A good procedure to follow in testing is as outlined by Garner.[2] The moisture is determined by heating 1 g. at 110° for four hours. Absence of moisture may indicate too friable a condition, so that the gum may powder too readily. The dried sample is then ignited, when the ash content should be less than 3 per cent. A larger value would indicate mineral addition. The ash consists mainly of the carbonates of calcium and magnesium. According to Garner the most important test in the evaluation of gum is the viscosity test and he recommends the following method in carrying it out.

4 g. of a typical sample of tragacanth is added to 50 ml. water and allowed to steep for two days. The volume is then made up to 500 ml. and the liquid passed through fine muslin. The resulting sieved mucilage is allowed to stand for an hour to become homogeneous. The viscosity is then determined in the usual way with a Redwood's viscometer. The calculations are as follows :—

[1] *Apoth. Zeit.*, 1890, 628.
[2] *Industrial Chemist*, 1927, 3, 34.

A is standard sample at P shillings per cwt. B is outside sample at Q shillings per cwt. 50 ml. of an a per cent. solution of A takes x secs. 50 ml. of a b per cent. solution of B takes y secs. Then 100 parts by weight of A give the same viscosity as $\frac{100bx}{ay}$ parts of B, and hence the equivalent weight of B to give the same viscosity as 100 parts of A should cost $\frac{Qbx}{ay}$ shillings. This relation only holds when the difference between x and y is only a few seconds.

3. Dextrin [1]

Dextrin is obtained by the treatment of starch with dilute acids, or by prolonged heating of the mixture with water to from 200° to 250°. It forms a white, yellow, or brown powder, according to the method of preparation and the temperature employed, and should be completely soluble in water. The solution is optically active; its specific rotation $[\alpha]$ is approximately $+200$. Several varieties of dextrin are known. Variation in the treatment of the starch breaks down the complex polysaccharide to various stages, so that the term dextrin does not represent a single substance. The more drastic breakdown gives products which do not give a reddish-brown colour with iodine. The presence of any maltose, which is recognizable by its sweet taste, renders the dextrin useless for the manufacture of matches, since maltose makes the match-heads hygroscopic and ultimately incapable of ignition. White dextrin is almost useless for this purpose, the most suitable apparently being of a light brown colour. Dextrin should not be hygroscopic; it should be inodorous, insipid in taste, and should form a mobile powder which is easily soluble in water. Dextrin is insoluble in alcohol.

The aqueous solution should be colourless, completely clear, and neither acid nor alkaline. It should give no blue or violet colour with iodine solution, no turbidity with lime water, and no precipitate with tannic acid and baryta water (soluble starch), or with lead acetate. When heated on platinum foil, it should burn without any residue. A blue or violet coloration with iodine indicates unaltered starch or soluble starch. The presence of lime is detected by the addition of ammonium oxalate, oxalic acid by lime water, gum arabic or mucilage by lead acetate. It does not form an osazone with phenylhydrazine.

Hanofsky recommends the following procedure for testing commercial dextrin :—

1. *Determination of the Constituents Soluble in Cold Water.* 25 g. of the substance shaken with cold water in a flask of 500 ml. capacity, filled to the mark allowed to settle, filtered through a folded filter and the solution used for the determination of maltose,

[1] See also *Analyst*, 1938, **63**, 697.

dextrin, and acidity. The maltose is best determined gravimetrically by Fehling's solution, the solution being boiled for five minutes. The solution is diluted to a quarter of its original strength (10 ml. Fehling's solution and 40 ml. water). A preliminary determination is made, to determine how much of the solution is necessary to reduce 10 ml. of Fehling's solution, and in the second determination, 1 to 2 ml. less than this quantity are taken and diluted until the whole volume is 57 to 58 ml.; 113 parts of copper correspond to 100 parts of anhydrous maltose; hence, when the solution is diluted to one-fourth, 113 parts of copper correspond to 91·3 parts maltose, or 1 part of copper corresponds to 0·80 part of maltose, from which the content of maltose M per 100 g. of the original substance is calculated. For the determination of the dextrin, 50 ml. of the solution (or 100 ml. if the quantity of insoluble matter is large) are diluted to 200 ml. and boiled gently under a reflux condenser with 15 ml. of hydrochloric acid of sp. gr. 1·125 for two hours. The liquid is then neutralised in a flask of 300 or 500 ml. capacity, diluted to the mark, and the dextrose determined with Fehling's solution. If the quantity of dextrose found in 100 g. of substance is D, the quantity of dextrin present in the original substance is 0·9 (D—1·05 M), since 20 parts of dextrose correspond to 19 parts of maltose. The acidity is determined by titrating 50 ml. of the solution with $N/10$ potassium hydroxide, using phenolphthalein as indicator. A certain error is introduced, if the volume of the residue in the flask is neglected, but in most cases it is unnecessary to take this into account. If, however, the quantity of insoluble matter is very great, a correction should be applied. If the sp. gr. of the residual starch be assumed to be 1·6, the volume of liquid to be deducted from 500 ml. is, $V = \frac{p}{1 \cdot 6}$, where p is the quantity of starch in 25 g. of substance. If the quantity of starch is 40 per cent., this volume is only 6·2 ml.

2. *Determination of the Insoluble Matter.* This consists almost exclusively of starch. 2½ to 3 g. of substance is boiled gently for two hours with 200 ml. of water and 15 ml. of hydrochloric acid of sp. gr. 1·125, whereby starch, dextrin and maltose are converted into dextrose. The dextrose is determined with Fehling's solution after neutralizing and diluting to 300 or 500 ml. If the quantity of dextrose found for 100 g. substance is D_1, the percentage of starch is calculated as 0·9 $(D_1 - D)$.

If the moisture, determined by drying at 110°, is W per cent., and the ash A per cent., the quantity of "other organic compounds" is :—

$$100 - (\text{maltose} + \text{dextrin} + \text{starch} + W + A).$$

W. Jettel obtained the following results in several dextrins by this method :—

	Maltose.	Dextrin.	Starch.	Water.	Ash.	Other organic compounds.	Acidity. ml. $N/10$ potassium hydroxide.
I.	4·25	47·78	35·55	10·11	0·27	2·04	40·0
II.	10·90	36·75	43·20	7·02	0·39	1·74	26·6
III.	3·75	29·46	58·00	6·85	0·60	1·34	25·3

Undecomposed starch may be detected microscopically and by its insolubility in water. There is generally a small amount of reducing material present from maltose, etc. It may be estimated by Fehling's solution.

It is very difficult to wash dextrin free from starch, and filtration is slow. In any analytical method which involves these operations special precautions must be taken or results are unreliable. A practical method for the determination of dextrin gum has been devised by Babington, Tingle and Watson,[1] which is comparatively rapid and accurate, within 5 per cent. with most commercial samples. The sample (1 g.) is warmed in a 100 ml. graduated flask with 30 ml. of water until just gelatinized and then rapidly cooled. 50 ml. of a cold saturated solution of barium hydroxide is next added and the volume made up to 100 ml. 50 ml. of the filtered solution is placed in a platinum dish. After the addition of 2 drops of a 1 per cent. phenolphthalein solution, $N/1$ hydrochloric acid is added to neutralization point. A faint pink colour is restored by adding two or three drops of the barium hydroxide solution. Approximately 10 g. of sand is added and the dish heated on a water-bath. The sand should be stirred when almost dry, to expose the maximum surface to the air, after which the dish is transferred to a well-regulated oven and dried to constant weight at 120°. The dish is now heated strongly to burn the organic matter completely. The dish is then cooled and weighed. The difference in weight before and after ignition represents the dextrin gum in 50 ml. of filtrate.

TESTING AND DIFFERENTIATION OF GUM ARABIC, GUM SENEGAL, AND DEXTRIN

Liebermann[2] gives the following procedure for this purpose :—

1. External examination of gum arabic which has not been artificially powdered.
2. External examination of gum senegal.

[1] *J. Soc. Chem. Ind.*, 1918, **37**, 257 T.

[2] *Chem. Zeit.*, 1890, **14**, 665.

3. Both forms of gum are completely soluble in water ; only particles of wood remain behind, which are generally reddish in the case of gum arabic, and blackish in the case of gum senegal. These particles of wood are found even in very pure specimens of gum. Other varieties of gum, as, for instance, that of the cherry tree, dissolve only partially in water. A swollen mass remains behind, which dissolves only on prolonged boiling or very long digestion.

4. The aqueous solutions of both sorts of gum give a bluish precipitate with potassium hydroxide and a few drops of copper sulphate ; but this is much more pronounced in the case of gum arabic, and collects in large flakes which rise to the surface in the test-tube, whereas the precipitate obtained with gum senegal is less pronounced, and consists of small flocculi, which remain more uniformly distributed throughout the liquid. These precipitates dissolve but slightly on warming, and no reduction occurs even on vigorous boiling.

5. Solutions of dextrin also give bluish precipitates with potassium hydroxide and copper sulphate, which do not dissolve on shaking in the cold, but dissolve completely on heating, giving rise to clear, dark blue liquids. On boiling for some time, complete reduction of the copper oxide occurs.

6. On prolonged heating with dilute potassium hydroxide in a test-tube, solutions of gum arabic and dextrin become amber yellow, whereas solutions of gum senegal are scarcely coloured, or assume only a faint yellow tint.

7. Mixtures of gum arabic and gum senegal behave towards potassium hydroxide and copper sulphate solution in the same way as gum senegal alone ; on boiling with potassium hydroxide alone, however, they behave like gum arabic solutions, the liquid becoming amber yellow.

8. Solutions of mixtures consisting of gum arabic and dextrin behave like gum arabic towards potassium hydroxide and copper sulphate, as regards the appearance of the precipitate. On boiling for some time, however, reduction takes place, if the quantity of dextrin is not too small. The same applies to mixtures of gum senegal and dextrin.

9. If the quantity of dextrin be too small, the reduction may not take place. In such cases the precipitate obtained with potassium hydroxide and copper sulphate must be filtered off, after moderate warming. The filtrate, which contains no gum, but is still somewhat milky and turbid, is boiled. A distinct separation of red cuprous oxide (or yellow hydroxide) shows the presence of dextrin.

10. The separation must be carried out in the same way, when mixtures of both sorts of gum with dextrin are under investigation. The copper precipitate, containing the acid gum products, is washed with distilled water, dissolved in hydrochloric acid, and this solution

precipitated with excess of alcohol. The precipitate is allowed to subside for one and a half to two days, the liquid then decanted and the transparent disc of gum, which remains at the bottom of the vessel, washed with alcohol. The small quantity of alcohol remaining behind is allowed to evaporate ; or, the gum is dissolved directly in hot water and the aqueous solution tested for gum arabic or gum senegal, as indicated in Nos. 4, 6, and 7.

Lead sub-acetate precipitates gum arabic in aqueous solution. In presence of sugar, addition of alcohol prevents the precipitation of dextrin if the latter is present. A quantitative separation of dextrins from gum arabic has been worked out from this reaction by André Hamy.[1]

The Examination of Gum Arabic can also be carried out as follows :—

A. Appearance of the gum, according to 1 and 2, if the gum has not been pulverized.

B. Solution of the powdered substance in lukewarm water. Observations as in No. 3. If the substance dissolves only partially, leaving a swollen gelatinous mass, it consists of cherry gum or a similar "gummi nostras," or of a mixture containing such gums. If the substance dissolves, all but a turbidity and a few particles of wood, proceed to :—

C. The aqueous solution is treated with excess of potassium hydroxide and some copper sulphate, gently warmed, and filtered :—

(a) *The Filtrate*, which may contain dextrin, is tested according to No. 9.

(b) *The Precipitate* is examined as in No. 10. If the aqueous solution of gum acids, prepared as described in No. 10, be treated with an excess of potassium hydroxide and some copper sulphate added, a precipitate results, which either agglomerates and rises to the surface, or remains in the form of small flakes uniformly suspended throughout the liquid.

Precipitate Agglomerates.	*Precipitate does not Agglomerate.*	
Gum arabic. (The aqueous solution becomes amber yellow on treatment with potassium hydroxide.)	Gum senegal, or a mixture of gum senegal and gum arabic. (The aqueous solution is boiled with potassium hydroxide.)	
	Amber Yellow Colour.	*No Colour, or Pale Yellow.*
	Mixture of gum arabic and gum senegal.	Gum senegal.

[1] *Ann. Falsif.*, 1929, **22**, 24-26.

In Thevenon's test[1] for gum tragacanth the presence of 5 per cent. gum arabic in gum tragacanth can be observed. A small amount of the mixture is warmed with water and an equal volume of 4 per cent. pyramidon solution added, followed by 10 drops of hydrogen peroxide (12 per cent.). In 5 to 30 minutes a blue colour develops, depending upon the amount of gum arabic in the sample. For quantitative tests a control is done with gum tragacanth of known purity with varying amounts of gum arabic present.

Detection of Gum Substitutes.[2] Many good, strongly adhesive gums have come on the market only in small quantities. As a consequence, substitutes have been exported in large quantities from South America, Australia, etc. Some of these have served the purposes of gum satisfactorily for some technical uses ; they proved to be easily soluble, but were all inferior to genuine gum arabic in adhesiveness. Some kinds, however, although of inviting appearance, proved to be quite insoluble, only swelling up when placed in hot water. It has been pointed out[3] that such gums could be rendered soluble by boiling under high pressure. This is probably correct, but gum so dissolved possesses a very inferior adhesive power, not even equal to that of starch paste ; it could therefore be used only for thickening ; even in this case starch or tragacanth is greatly preferable.

When such gum substitutes come in the unmixed state into the market, they are easily recognized ; but when ground to a coarse powder, and mixed with an equal part of genuine gum gheziri, a simple solution test does not show the presence of substitutes, since the swollen gelatinous particles of the substitute remain suspended, and are completely invisible. In order to detect such adulteration with certainty, the following simple method may be recommended.

The suspected gum is covered with ten times its quantity of hot water, and allowed to stand for three or four hours, with frequent stirring. When the insoluble matter has subsided, half the liquid is poured off, replaced by the same quantity of cold water, and again well stirred. This process is repeated twice within an hour. The last mixture separates after short standing into two parts, the upper layer consisting of water, and the lower layer of a gelatinous, highly refractive mass. In this way, the presence of even 5 per cent. of adulterant can be detected with certainty.

4. Other Adhesives

Among substances which have been suggested as adhesives are (*a*) casein (B.P. 362001/1930; U.S. Pat. 1886750/1933), (*b*) rubber

[1] *Ann. Falsif.*, 1920, 13, 489. [2] *Cf.* A. Jaksch, *Chem. Zeit.*, 1891, 15, 77.

[3] Robinson, *Rep. Brit. Ass.*, 1906, 227; *J. Soc. Dyes and Col.*, 1918, 34, 10; *Chemical Abstracts*, 1928, 1868, 3983.

latex (French Pat. 735348/1932), and (*c*) hydroxyalkyl ethers of carbohydrates (B.P. 389534/1933).

E. COLOURING MATTERS

Red lead, manganese dioxide, ochre, umber, smalt, ultramarine, and various coal-tar dyes are employed. For the analysis of the former, see Vol. II., pp. 491-555.

IV. Materials for the Striking Surface

These are the same as for the match compositions. Manganese dioxide, the sulphides of antimony, powdered charcoal, amorphous phosphorus, potassium chlorate, glass powder, etc., as frictional materials ; chalk, etc., as filling materials ; umber and the like as colouring matters ; glue, gelatin, and dextrin as binding materials.

V. Match Compositions [1]

A. COMPOSITIONS FOR MATCHES WHICH STRIKE ON ANY SURFACE

This class includes not only matches made with ordinary phosphorus, but also matches free from phosphorus, and those which contain red phosphorus, with or without sulphur and phosphorus sesquisulphide. For a great number of years attempts have been made to eliminate the use of phosphorus, and of special striking surfaces. Many of the proposed substitutes for phosphorus, however, have been too expensive, some too little inflammable, some too unstable, and some only available for paraffined matches.

In those match compositions which contain no white phosphorus, sulphur is mixed with such substances as amorphous phosphorus, phosphorus sesquisulphide, antimony sulphide, thiocyanates, and cyanides of metals, etc. ; or, easily inflammable substances, like charcoal, the salts of fatty acids (stearates), carbon compounds, such as naphthalene and phenanthrene, as well as shellac and resins. As oxidizing agents, besides those already mentioned, such as potassium permanganate and nitro-compounds, gun-cotton, aromatic nitro-compounds, such as trinitrophenol (picric acid) and picrates, have been tried. These last substances are explosives ; their properties are described in the section on Explosives (p. 531). Chlorates and perchlorates have also been used as oxidizing agents in match compositions. So as to retard the combustion and to ensure a complete ignition of the composition, a small quantity of a complex metallic cyanide, such as

[1] For further details, see Ludwig Metz, *Chemische Untersuchung der Spreng- und Zündstoffe*, Braunschweig, 1931.

Prussian blue, Turnbull's blue, or even the material used in gas purification, is added; this contains free sulphur, thiocyanates, and complex metallic cyanides.

Rossel gives the following two recipes for the preparation of match compositions: (1) 10 parts of potassium chlorate, 7 parts of pure and freshly precipitated lead thiosulphate, 2·5 to 2·9 parts of antimony trisulphide, 0·25 parts of gelatin. (2) 300 parts of powdered glass, 120 parts of manganese dioxide, 160 parts of potassium dichromate, and 90 parts of flowers of sulphur; these are mixed together in water and finely ground. In another case 300 parts of gum arabic and 210 parts of glue are dissolved in water, and 1800 parts of well-powdered and sieved potassium chlorate are added; the following substances are then added consecutively, each being finely powdered: 600 parts of lead thiosulphate, 450 parts of red lead, and 25 parts of barium thiosulphate. Rossel gives particulars also of the following composition, containing red phosphorus: 450 parts of potassium chlorate, 100 parts of potassium dichromate, 75 parts of powdered glass, and 60 parts of sulphur (washed flowers of sulphur or powdered roll-sulphur), 25 parts of *caput mortuum* (iron oxide), 7 to 8 parts of red amorphous phosphorus, 110 parts of gum arabic, and 30 parts of gum tragacanth.

Craveri [1] has proposed the use of persulphocyanic acid, which is supposed not to react when hammered or rubbed, is claimed to be non-poisonous and harmless during the manufacture of the match compositions, and cheaper than phosphorus.

The composition made by Bohy, Gallay, & Co., of Nyon,[2] contains salts of hypophosphorous acid, mainly the calcium salt, in place of ordinary or amorphous phosphorus. Calcium, barium, and strontium hypophosphite ignite only at a high temperature; if, however, they are mixed with potassium chlorate or nitrate, or any other oxidizing agent, ignition takes place very readily. This composition is made as follows: 210 g. of glue and 30 g. of gum tragacanth are allowed to soften for twelve hours in water, then warmed and boiled; 25 g. of turpentine is added, then 1 kg. of potassium chlorate, 200 g. of sulphur, 150 to 200 g. of a hypophosphite (calcium, barium, or strontium salt), 5 to 10 g. of potassium dichromate, 125 to 150 g. of barium chromate, 200 to 250 g. of powdered glass, and 10 g. of colouring matter. Another composition can be obtained by the further addition of 150 g. of naphthol yellow, or in place of this, 100 g. of picric acid.

Another match composition [3] is made up of barium chlorate, sulphur, inert matter, and a binder, the amount of barium chromate being approximately twice that of the potassium chlorate.

[1] Eng. Pats. 18563 and 27520/1897.
[2] Eng. Pat. 16037/1898; Ger. Pat. 106734 f.
[3] U.S. Pat. 1290146/1919.

Even before Sévène and Cahen, Rals [1] had recommended fusing together sulphur and red phosphorus, but the result was not equivalent to phosphorus sesquisulphide. The Sévène-Cahen process was taken up by the French Government, and it is said that the French public did not notice any difference, on the introduction of the so-called " S. and C." matches, containing this substitute for phosphorus.

The " S. and C." composition varies, according to whether it is to be used for paraffined or sulphured splints, or for waxed threads. The ordinary composition is as follows: 6 parts of phosphorus sesquisulphide, 24 parts of potassium chlorate, 6 parts of zinc oxide (zinc white), 6 parts of red ochre, 6 parts of powdered glass, 6 parts of glue, and 34 parts of water. It is easy, by manipulation, to make these matches either more or less inflammable. The mechanical processes are much the same as in the manufacture of phosphorous matches.

In Aronson's composition [2] a small proportion of potassium oxy-salts are used with a relatively large proportion of phosphorus mixed with an equal proportion of lamp-black or other non-glowing material, and binding agent (dextrin).

The Chemische Fabrik Griesheim-Elektron has placed on the market a product,[3] called " Sulfophosphit," which consists of zinc, phosphorus, and sulphur. It is stated that both paraffined and sulphured matches can be made with this substance, with any required degree of inflammability. " Sulfophosphit " is claimed to be more stable, under atmospheric influences, than red phosphorus and phosphorus sesquisulphide; also, the price is alleged to be low.[4]

The basis of another dipping composition, made by R. Gans,[5] is a mixture of " sulfocuprobariumpolythionate " and potassium chlorate. The composition is said to be comparatively insensitive to warmth, and to keep for a long time. The splints, after dipping, are coated with a spirit or water varnish. This new composition is said to be more inflammable than that of Schwiening.

B. COMPOSITIONS FOR SAFETY-MATCHES WHICH REQUIRE A SPECIAL STRIKING SURFACE

Brown Safety-Match Composition (Kellner). 150 parts of gum senegal are dissolved in 200 parts of water, and at the same time 20 parts of powdered tragacanth are digested in 300 parts of water for twenty-four hours; these solutions are united and boiled, and 100 parts of powdered and sifted potassium chlorate introduced. To

[1] Ger. Pat. 89700.
[2] U.S. Pat. 1287819/1919.
[3] Ger. Pat. 153188/1902.
[4] Cf. *Allgem. Chem. Zeit.*, 1906, p. 207.
[5] Ger. Pat. 157424/1903.

this is added a finely powdered and thoroughly mixed mixture of 125 parts of potassium dichromate, 30 parts of sulphur (crushed roll-sulphur or washed flowers of sulphur), 33 parts of antimony trisulphide, 50 parts of powdered colophony, 200 parts of minium or of lead peroxide, 100 parts of umber or terra di Sienna, 100 parts of powdered glass or powdered pumice stone, and lastly 150 parts of hot water.

Composition for the Striking Surface. 400 parts of dextrin are mixed with 400 parts of water, boiled, and allowed to cool; with this is mixed a thin paste of red phosphorus, which has been made by stirring 1000 parts of red phosphorus with 2000 parts of water, allowing to stand, and pouring off the excess of water. Then 200 parts of prepared chalk (the mass swells up, owing to evolution of carbon dioxide), 300 parts of umber, and 1000 parts of finest powdered antimony sulphide are added, and the whole mixture passed through a mill.

Rossel used the following composition: 10 parts of gum arabic, 300 parts of gum tragacanth, 53·8 parts of potassium chlorate, 6 parts of *caput mortuum*, 12 parts of powdered glass, 5 parts of potassium dichromate, 3 parts of sulphur, 1·2 parts of chalk or colophony, and 6 parts of manganese dioxide. The striking surface for this composition consisted of 5 parts of antimony sulphide, 3 parts of amorphous phosphorus, 1½ parts of manganese dioxide, and 4 parts of glue.[1]

Moisture-proof striking surfaces are formed by mixing the active substances with a solution in an organic solvent of a hardening insoluble non-combustible binding agent.[2]

A phosphorus-free striking surface, recommended by Craveri,[3] on which any safety-match will ignite, is made up as follows: 2 parts of a thiocyanate compound, 1 part of persulphocyanic acid, 0·5 part of potassium xanthate, 4 parts of antimony sulphide, and as a binding material, 1 part of gelatin.

Many different types of matches or match substitutes have been suggested from time to time, but they have not come into general use. As one example of this type, reference may be made to "rods" capable of ignition by friction.[4] The rods can be extinguished and re-ignited repeatedly. They comprise a foundation of organic substances, ash free and having a speed of combustion less than that of a low nitrated cellulose. A typical mixture of this class consists of cellulose nitrate or acetate mixed with ammonium oxalate, camphor, or naphthalene and an ignition mixture free from phosphorus (*e.g.* potassium chlorate and sulphur). Additional substances, as binders, combustion regulators, filters, pigments, etc., may also be added.

[1] Jacobsen, *Chem. techn. Repertorium*, 1881, 1, 150.
[2] Swed. Pat. 86737 (1936).
[3] Ger. Pat. 114279.
[4] B.P. 329796/1929.

VI. The Chemical Examination of Match Compositions

The composition, when examined under the magnifying glass, should be as uniform as possible, and it is important that no particles of phosphorus should be visible.

The following method of examination is recommended by Bolley,[1] for the purpose of determining the constituents of a match composition. The matches are placed in water at a maximum temperature of 20°, in a porcelain basin, the swollen heads removed by mechanical means, and after having been broken up under the water, digested and continually stirred (in the absence of phosphorus, the mixture can be boiled), and then separated by filtration.

1. The filtrate, which may contain potassium chlorate, potassium nitrate, lead nitrate, potassium chromate, potassium ferrocyanide, gum, glue, and dextrin, as well as other substances that are soluble in water, is divided into several portions. One of these is tested for lead, another for chlorate. Another portion is evaporated and ignited ; if the residue, on moistening, gives an alkaline reaction, a nitrate is present. Ferrocyanic acid is tested for with a ferric salt. To determine the presence of gum or glue, a rather larger portion of the same filtrate is evaporated to dryness with sodium hydroxide ; on heating a portion of this residue in a tube, the presence of glue or albuminous matter is indicated by the evolution of ammonia gas, which can be tested for in the usual manner, either by smell, or with hydrochloric acid, or with turmeric paper. Gum and glue are precipitated from the solution on addition of alcohol. The presence of dextrin in the solution is determined by the addition of a few drops of a solution of iodine, when a pale reddish-blue coloration is formed.

2. The residue on the filter paper is digested with alcohol, so as to extract stearic acid, paraffin, and resins. To extract wax, it is necessary to boil with the alcohol ; this is not permissible, however, in the presence of phosphorus. The alcoholic filtrate, after evaporation, yields a substance, from the consistency, melting point, etc. (solubility in ether, fractional crystallization, and melting point), of which conclusions can be drawn as to the nature of the residue. If phosphorus is present in the residue it can be removed before the digestion with alcohol, by treatment with nitric acid to convert it into phosphoric acid, which is recognizable by the usual means.

Matches containing phosphorus become luminescent in the dark, and when moistened with water, give the characteristic smell of phosphorus.

3. The original residue, which remains after the digestion with water, will evolve chlorine on heating with hydrochloric acid, if lead

[1] *Cf.* Muspratt's *Handbuch der technischen Chemie*, vol. x.

peroxide, red lead, or manganese dioxide be present ; the smell of sulphurous acid denotes sulphites, and lead, manganese, iron, and antimony can be tested for in the residual solution. The presence of lead peroxide, or of red lead, is recognized from the colour of the match-head. Ochre remains partly, and smalt completely, undissolved ; both can be recognized with the blowpipe, whereas ultramarine is decomposed by hydrochloric acid, evolving sulphuretted hydrogen. Charcoal, sand, and powdered glass remain undissolved in hydrochloric acid, and can be identified with a magnifying glass ; sulphur can be recognized by its colour, by the smell on burning, or it can be extracted with carbon disulphide.

A. EXAMINATION FOR PHOSPHORUS

The recognition of phosphorus is very much simplified by its luminosity in the dark ; but with a small quantity of phosphorus in a very large quantity of matter, for instance, in poisoning cases, either in a quantity of food, or in the stomach contents, this luminescence does not show, even when friction is applied. The material is firstly examined for an odour of phosphuretted hydrogen or of ozone, which would denote the presence of free phosphorus. It should be examined by Scherer's test as follows :—Strips of paper, soaked respectively in a 5 per cent. silver salt solution and in an alkaline lead solution (5 per cent.), are hung up over the material for examination. If phosphorus is present, the silver paper only will be blackened ; should both papers turn black, the presence of sulphuretted hydrogen is proved, but not the presence of phosphorus ; that is to say, this test for phosphorus fails in the presence of sulphuretted hydrogen. Even when a positive test is obtained the results must be confirmed otherwise, preferably by Mitscherlich's test. Attempts can also be made, by treating the matter with water, to collect any minute floating particles of phosphorus in a filter, and if this is successful, they can be oxidized by nitric acid to phosphoric acid and tested for in the usual way. The material may also be treated with a small amount of benzene and a strip of paper 10 cm. by 3 cm. soaked in it. This is then suspended in a glass tube connected to a Victor Meyer's heating apparatus and exposed to a current of air at 40° to 50°. Even when the benzene solution contains not more than 0·01 mg. of white phosphorus per ml. the paper will become luminescent when examined in the dark.[1]

The following method, however, due to Mitscherlich, is satisfactory :—The mass is acidified with sulphuric acid, and distilled with steam, the vapours being passed through a vertical condenser ; if

[1] Schröder, *Arbeiten aus dem Kaiserlichen Gesundheitsamt*, 1913, 44 ; *Chem. Soc. Abs.*, 1913 (ii.), 618.

phosphorus is present, it is vaporized with the steam, and can be recognized as a luminescent ring, which moves up and down in the condenser. The test is conducted in a darkened room; it is possible by this means to detect 0·00001 parts of phosphorus. It is often possible to find small particles of phosphorus in the distillate, and to obtain the test for phosphorous acid. The phosphorus and phosphorous acid are treated separately with strong chlorine water, and thus oxidized to phosphoric acid, which is estimated in the usual manner with magnesia mixture, as ammonium magnesium phosphate.

Care must be taken in carrying out this test that alcohol and ether, should they be present, do not prevent the luminescence of the vapours. Turpentine and other volatile oils, as well as phenol and creosote, often completely prevent it; furthermore, red phosphorus does not produce this luminescence, but mixtures of sulphur and phosphorus, such as are found in match-heads, will cause it. According to Polstorff and Mensching,[1] the luminescence is also hindered by the presence of mercury salts. Copper salts and sulphuretted hydrogen also are said to interfere. Even after continued distillation, the whole of the phosphorus will not be found in the distillate; O. Schifferdecker calculates that for every milligram of phosphorus in the distillate, the original substance contained 1·5 to 2·0 mg.

According to K. Fischer,[2] the presence of potassium chlorate in match compositions greatly interferes with the testing for phosphorus, and it is advisable to wash the sample several times with cold water to eliminate the chlorate, before distilling. If substances soluble in water are to be determined, the two tests can be combined. The washing with water can be avoided by using tartaric acid for the distillation instead of sulphuric acid; the presence of potassium chlorate does not then influence the phosphorus test.

Another means of detecting phosphorus, described by Dusart [3] and Bloudlot,[4] is based on the fact that small quantities of phosphorus, phosphorous acid and silver phosphide, give with nascent hydrogen, phosphuretted hydrogen, which can be recognized by the emerald green colour imparted to the hydrogen flame when a porcelain basin is held in it. The hydrogen must be free from sulphuretted hydrogen, and must be passed through a tube containing pumice-stone soaked in potassium hydroxide, before lighting, otherwise the flame would appear blue; the gas exit tube should have a platinum-covered tip, as the sodium contents of the glass will otherwise colour the flame. The substances containing phosphorus must not be introduced directly

[1] *Ber.*, 1886, **19**, 1763.
[2] *Arbeiten aus dem Kaiserlichen Gesundheitsamt*, **19**, 307.
[3] *Jahresber. d. Chemie*, 1856, 724.
[4] *Ibid.*, 1861, 821; *Z. anal. Chem.*, 1861, **1**, 129.

into the hydrogen-generating mixture, as they easily prevent the formation of the green flame. But the phosphorous acid or phosphorus particles obtained by Mitscherlich's test can be introduced into a suitable mixture of zinc and dilute sulphuric acid ; or silver phosphide, which is obtained as a black powder by heating the acidified phosphorus-containing matter in a current of carbon dioxide, and passing the gas into a solution of silver nitrate, may be so introduced. The green flame appears in the presence of the smallest trace of phosphorus, and, according to Christofle and Beilstein, gives a spectrum with three green lines, of which the two strongest are in the green, and the weakest in the yellow. Dusart's test has been modified by Dalmon in such a manner that the whole of the organic matter containing phosphorus is treated with hydrogen. The gas is passed through a long drawn-out glass tube, bent upwards at right angles, and is lighted at the end ; if a narrow glass tube is pushed over the jet, the flame shortens, and appears green, for the whole length of the tube, and when the tube is pushed down further, the flame shortens still more, becomes dark blue, and if the glass tube is slowly drawn away at this moment, a magnificent emerald-green flame-ring appears, passing up the tube with greater or less velocity. The phosphorus-charged hydrogen, generated in this way, luminesces in a dark room, without the gas being ignited.

In Schloesing's test [1] for free white phosphorus in phosphorus sesquisulphide the latter is shaken with light petroleum (b.p. 45°) to dissolve free phosphorus. The liquid is quickly filtered and an aliquot part evaporated in a vacuum at 15° to 20°. The residue is oxidized with nitric acid and the phosphorus estimated. In order simply to detect the presence of phosphorus, the residue after evaporating off the petroleum is shaken with fine sand in a flask in the dark and carefully examined for phosphorescent glow.

Other methods for the detection of phosphorus in mixtures have been described by Nicklès [2] and Bastelaer [3] and Lemkes.[4]

With regard to the period during which phosphorus will remain in organic matter and can be tested for, Medicus [5] gives the following data :—Neumann found phosphorus in a corpse after it had been buried for fourteen days. Dragendorff mentions a case, in which he was able to detect phosphorus in the secretions in a corpse that had been buried for several weeks and afterwards exhumed. Fischer and Müller were able to detect phosphorus in the body of a guinea-pig, which had been buried for eight weeks. On the other hand, Herapath was unable to detect a trace of phosphorus twenty-three days after

[1] *Compt. rend.*, 1912, **155**, 1461. [2] *Z. anal. Chem.*, 1870, **9**, 71.
[3] *N. Jahresber. d. Pharm.*, **40**, 24. [4] *Pharm. Weekblad.*, 1916, **53**, 1496.
[5] *Z. anal. Chem.*, 1880, **19**, 164.

death ; Brandes could find no phosphorus in the corpse of a child after three weeks, but could detect its acids. Medicus was able to detect phosphorus for half an hour by Mitscherlich's test twenty-three days after poisoning ; the sulphuric acid solution, after filtering, gave a gas containing phosphorus on treatment with zinc and hydrochloric acid.

B. TESTING FOR ORDINARY PHOSPHORUS IN MATCH-HEADS

Prohibition of the Use of White Phosphorus.—Subsequent to conferences held at Berne in 1905-6, certain European countries discontinued the use of white phosphorus in the manufacture of matches. In Germany a law that white phosphorus should cease to be used for the manufacture of matches after 1st January 1907 was approved. In the United Kingdom the " White Phosphorus Matches Prohibition Act (8 Edward VII., 1908, chapter 42) " was passed on 21st December 1908, and came into force on 1st January 1910.[1] According to this Act :—" It shall not be lawful for any person to use white phosphorus in the manufacture of matches, and any factory in which white phosphorus is so used shall be deemed to be a factory not kept in conformity with the Factory and Workshop Act, 1901. . . . It shall not be lawful for any person to sell or to offer or expose for sale . . . any matches made with white phosphorus. . . . It shall not be lawful to import into the United Kingdom matches made with white phosphorus, and matches so made shall be included among the goods enumerated and described in the table of prohibitions and restrictions contained in section 42 of the Customs Consolidated Act, 1876."

Detection of White Phosphorus.—It is now necessary, therefore, to test for white phosphorus in match-heads, in cases where its presence is suspected. Hitherto no exact method has been advanced, suitable for the detection of white phosphorus under all conditions.

On the one hand, the examination of phosphorus sesquisulphide, which is frequently present, is, according to Friedheim,[2] difficult, because the sulphur-phosphorus compounds gradually decompose into compounds containing less sulphur, with separation of white phosphorus, and on the other hand, the detection of phosphorus in matches in presence of potassium chlorate cannot be carried out by the ordinary methods of analysis.

In some cases it is possible, when examining match-heads stated to contain no white phosphorus, and to which no white phosphorus has been added as such, to demonstrate the presence of this substance, yet it cannot be ascertained whether it was added, or whether it was

[1] Cf. *J. Soc. Chem. Ind.*, 1909, **28**, 43.

[2] *International Congress for Applied Chemistry*, V., Berlin, 1903.

re-formed from phosphorus sesquisulphide. Again, in other cases, no phosphorus may be detectable, notwithstanding its presence, because the test sometimes fails in presence of potassium chlorate (*cf.* p. 623).

To test for ordinary phosphorus, at least twenty-five match-heads are placed directly in a Mitscherlich apparatus, with 50 ml. of water and 10 ml. of dilute sulphuric acid. The mixture is heated over a flame, without the introduction of steam (*cf.* p. 622); if potassium chlorate is present, the phosphorescence may not appear (*cf.* p. 623); but on the other hand, phosphorus sulphide is capable of producing a luminescence which, though different from that caused by phosphorus, may be mistaken for it.[1] In the first case, either the substances soluble in water, including the potassium chlorate, must first be removed from the match-heads with cold water, or the test must be carried out with tartaric acid. To determine the presence of very small amounts of yellow phosphorus in red phosphorus the following test has been proposed by Kray [2]:—

20 g. of the red phosphorus product is dissolved in 30 ml. of carbon disulphide and filtered. Part of the filtrate is tested with filter paper which has been impregnated with copper sulphate solution; the depth of the brown colour is a measure of the amount of yellow phosphorus present.

To test for ordinary phosphorus in the presence of phosphorus sulphide (phosphorus sesquisulphide, P_4S_3), the following process, due to R. Schenck and E. Scharff,[3] can be employed. This method is based on the property of ordinary phosphorus, when oxidized to phosphorus trioxide, of ionizing the air, which then becomes capable of conducting electricity. Phosphorus and sulphur compounds, even if they luminesce, do not produce this effect.

The apparatus employed (Fig. 127) consists of two parts, connected by a glass tube, viz., the vessel *a*, for generating the phosphorized air, and the electroscope *b*. The former is a test-tube with a side connection, and a ground-glass stopper, through which the air delivery tube passes, reaching nearly to the bottom of the test-tube. A glass tube is attached to the side connection by means of rubber tubing, which delivers the phosphorized air to the cylindrical condenser *c*, the removable top *d* of which carries the electroscope. Within the outer cylinder *c* is an insulated cylindrical disperser (*Zerstreuungkörper*) suspended from the electroscope.

The phosphorus oxidation products are prevented from entering the inside of the electroscope case *b*, from *c*, by two insulated plates, which can be removed and cleaned, and through which the carrier of

[1] *Cf.* Mai and F. Schaffer, *Ber.*, 1903, **36**, 870; *cf.* E. G. Clayton, *Proc. Chem. Soc.*, 1902, **18**, 129; 1903, **19**, 231.

[2] *Ind. Eng. Chem.*, 1927, **19**, 826.

[3] *Ber.*, 1906, **39**, 1522.

the disperser passes and fits closely. A small piece of sodium is put in *c* to prevent access of moisture. A rod, by means of which the disperser can be charged, which is well insulated and has a properly insulated handle, passes through the lid of the cylinder *c*.

To charge the electroscope, the rod is pushed down close to the disperser, and Zamboni's dry pile brought up to it and then removed ; after charging, that is, when the aluminium leaves of the electroscope are apart, the rod is drawn up again.

To carry out the test, some of the match composition, for instance a few softened and ground match-heads, mixed with zinc oxide (to hold back sulphuretted hydrogen), are placed in the test-tube *a*, which

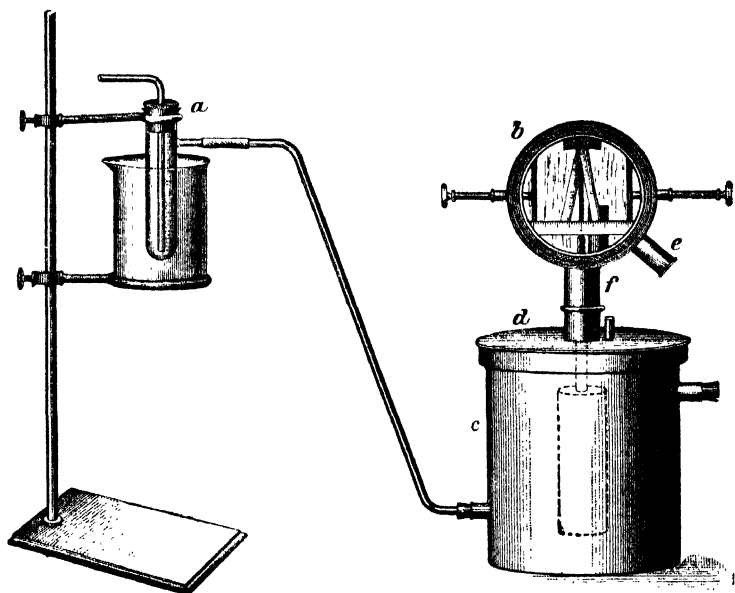



FIG. 127.

is surrounded by warm water at 50° ; after the electroscope has been charged, air is blown through about ten times successively with the aid of a rubber ball, or the air can be drawn through by connecting an aspirator, care being taken to place a bottle of several litres capacity, to catch any solid matter that might get sucked over, between the aspirator and *c*.

In the presence of the smallest quantities of ordinary phosphorus, the electroscope will be discharged, that is to say, the aluminium leaves fall together suddenly. Under normal conditions this takes place only slowly. The leaves ordinarily move through 0·2 to 0·5 divisions of the scale in five minutes.

The following method for the detection of white phosphorus in matches is based upon that of Aronstein. One hundred or more

match-heads are moistened with water, and then boiled with carbon disulphide for two hours under a reflux condenser. The cooled extract is filtered through a dry filter paper into another flask, and the carbon disulphide distilled off on a water-bath. The flask containing the residue is at once connected with an apparatus by which, firstly, carbon dioxide, and secondly, dry air can be introduced. While the current of carbon dioxide is driving off the small quantity of carbon disulphide remaining in the flask, the temperature of the water in which the flask is immersed is gradually raised from about 15° to 30°. The room having been previously darkened, dry air is admitted into the flask at different and increasing temperatures, the current of carbon dioxide meanwhile being almost entirely turned off. Careful watch is kept for any sign of luminescence. If there be none at 30°, the temperature is gradually raised. In most cases, when white phosphorus is present, luminescence is seen below 35° ; very occasionally it may first appear at as high a temperature as 55°. The glow temperatures observed in two experiments (December 1910), with matches containing white phosphorus, were 23° and 25° (E. G. Clayton). The lowest limit of glow for phosphorus sesquisulphide, in the absence of white phosphorus, is generally about 60°,[1] so that this process can be applied to the detection of small quantities of white phosphorus in the presence of considerable amounts of phosphorus sesquisulphide.

According to C. Van Eijk,[2] a tube containing phosphorus sesquisulphide is not luminescent below 70°, but if 0·02 per cent. of white phosphorus be present a glow appears below 60°. An alternative plan is to extract with carbon disulphide, evaporate off the solvent, and distil the residue with a solution of lead acetate. Sesquisulphide of phosphorus is decomposed, and luminescence appears only in the presence of white phosphorus.

T. E. Thorpe's Sublimation Test for white phosphorus is carried out as follows :—A few grams of the match-heads, or of the composition, are dried thoroughly over sulphuric acid in a desiccator filled with carbon dioxide, and transferred to a bulb of 25 ml. capacity blown on the end of a tube 20 cm. long and 15 mm. in diameter. Dry carbon dioxide is introduced, the apparatus evacuated as completely as possible, and the end sealed off. The bulb is then gently heated for two hours at from 40° to 60°. Phosphorus, if present, will be volatilized, and condensed in the upper part of the tube as a transparent, highly refractive sublimate of octahedral or dodecahedral crystals. It is claimed that this is the most trustworthy test for the presence of small quantities of ordinary phosphorus in the striking compositions of matches containing phosphorus sesquisulphide.

[1] In recent experiments, E. G. Clayton has observed a very faint luminescence at 50°.

[2] *Chem. Centr.*, 1906, 2, 358 ; *Chem. Weekblad.*, 1906, 3, 367, 404.

The test of Phelps [1] is more sensitive than the above for small quantities of phosphorus, and it is more rapid when a large number of samples require examination. It is based on the volatility of white phosphorus in a current of steam and its luminescence with oxygen. 0·1 mg. in 10 ml. of water can be detected. Hydrogen after washing with alkaline pyrogallol is passed into boiling water containing ten to twelve match-heads. The gas issues through a fine capillary at a relatively high velocity. The capillary is enclosed in a dark chamber and is viewed through a small microscope. The upper two inches of the capillary are heated electrically to prevent condensation. The method is applicable in the presence of nitrates, chlorates, hydrogen sulphide (phosphorus sesquisulphide), or carbon disulphide.

C. TESTS FOR CYANOGEN COMPOUNDS

When soluble cyanides or ferro- and ferri-cyanides are distilled in the presence of potassium chlorate, with sulphuric acid, free hydrocyanic acid is found in the distillate; insoluble substances of this nature, such as Prussian and Turnbull's blue, and "the spent oxide" of gasworks also are decomposed. Accordingly, when testing for cyanogen compounds, 1 g. of the scraped match-heads is treated with 50 ml. of warm water and filtered, and both the filtrate and the residue distilled separately with dilute sulphuric acid. Hydrocyanic acid can be identified in the distillate by the following reactions:—

1. *Prussian Blue Reaction.* To the distillate is added a drop of ferric chloride and a drop of ferrous sulphate solution, or only a drop of ferrous sulphate solution, as this generally contains a little of the ferric salt; this is then made alkaline with a little sodium or potassium hydroxide, well shaken and carefully acidified with hydrochloric acid. In the presence of hydrocyanic acid, a precipitate of Prussian blue is formed, or the liquid turns green and deposits blue flakes on standing.

2. *Thiocyanate Reaction* (Liebig). Another portion of the filtrate is evaporated on the steam-bath with sodium or potassium hydroxide and a little yellow ammonium sulphide; any hydrocyanic acid present is converted into sodium or potassium thiocyanate, which, when taken up with water and a little hydrochloric acid, gives a deep blood-red coloration on the addition of a drop of ferric chloride.

3. *Nitroprusside Reaction* (Vortmann [2]). To another portion of the distillate a few drops of potassium nitrite are added, then two to four drops of ferric chloride, and enough dilute sulphuric acid to convert the yellow-brown colour into pale yellow. The liquid is heated until it just begins to boil, cooled, a little ammonia added (enough to precipitate

[1] *U.S. Hyg. Labor. Bull.*, **96**, 51-54. [2] *Monatsh.*, 1886, **7**, 416.

the excess of iron), and filtered. Two drops of dilute, colourless ammonium sulphide are then added to the filtrate ; a violet coloration, changing to blue, green, and yellow, shows the presence of hydrocyanic acid. Very small quantities give only a bluish-green or a greenish-yellow coloration. This reaction is the reverse of the well-known nitroprusside test for sulphuretted hydrogen and alkali sulphides, and is based on the conversion of any cyanogen present into potassium nitroprusside, $K_2Fe(NO)(CN)_5$, which is a very delicate reagent for alkali sulphides.

4. *Silver Nitrate Reaction.* The distillate is treated with nitric acid and silver nitrate ; the presence of hydrocyanic acid is shown by a white precipitate, which should be stable to the light, and readily soluble in ammonia and potassium hydroxide.

D. QUANTITATIVE ANALYSIS OF MATCH COMPOSITIONS

The composition, without any previous softening with water, is carefully separated from the splints, with a sharp knife, care being taken to remove as little wood as possible, and weighed. Or the weight of the head can be estimated by drying several cut-off match-heads in a desiccator over sulphuric acid, and weighing them, then removing the heads with warm water, and drying and re-weighing the pieces of wood.

The estimation of free white phosphorus is carried out, as described on p. 625, and that of the other constituents by the usual methods. For the estimation of potassium chlorate, 0·5 g. of the composition is washed several times with 50 ml. of water, a little potassium iodide (free from iodine) added, and one and a half times the volume of fuming hydrochloric acid. The whole is heated in a closed bottle for fifteen to twenty minutes on the steam-bath, and when cold, the liberated iodine titrated with $N/10$ sodium thiosulphate.

VII. Physical Tests

A. INFLAMMABILITY ON STRIKING SURFACES

Swedish and other safety-matches are supposed to strike only on the prepared surfaces on their boxes, but as a matter of fact they will ignite on several striking surfaces, such as hard wood, smooth hard paper, fine grained and not quite smooth stones, glass, porcelain, etc.

For tests carried out in Germany,[1] the following materials were used :—A smooth board of beech wood 40 cm. long, a sheet of glass 40 cm. long, hard paper, the width of a match-box striking surface, 10 cm. and 20 cm. long, a fine grained plate of marble 15 cm. long, a

[1] *Arbeiten aus dem Kaiserlichen Gesundheitsamt.*

slightly rough iron plate 15 cm. long, rough glass paper 5 cm. long, and fine grained glass paper 10 cm. long. To apply the test, the match is drawn with an even, gentle pressure slowly over the surface.

B. TEMPERATURE OF IGNITION

To ascertain the exact temperature at which matches will ignite is extremely difficult, on account of the various necessary precautions, and because concordant results are not obtained when the work is carried out under the same conditions. The temperature at which they will inflame of their own accord, in the case of white phosphorus matches, for instance, is lower as the percentage of phosphorus rises, and is more or less dependent on the distribution of the phosphorus in the composition. The more evenly the phosphorus is distributed throughout the composition, the higher will be the temperature of ignition ; should a match-head contain a fairly large piece of phosphorus, it is possible for the temperature of ignition to be very little above that of phosphorus. On the other hand, it is known that, by continued careful heating in a current of air at about 70°, many kinds of matches lose their phosphorus, so that although the matches keep their shape and appearance, they are either almost unignitible or the temperature of ignition is found to be much higher than the real ignition temperature. Moreover, the better the matches have been varnished, the higher the temperature of ignition. The ignition point of badly varnished matches varies with the thickness of the coating. The temperature of ignition of any one class of goods can accordingly vary with the circumstances and the methods employed. A large number of tests should therefore be made, and an opinion given with very great care.

The apparatus used in Germany [1] consists of a double-walled, asbestos-covered aluminium box with a double-walled door, provided with a small pane of mica for the purpose of observation. It is provided with three tubes for thermometers, and for inserting the matches, which can be placed at any height inside the box. The apparatus is divided longitudinally inside into three sections by pieces of wire gauze, in the central one of which is placed the thermometer, and in the side ones the matches for testing. The wire gauze serves to protect the thermometer, as well as the neighbouring matches, from pieces of match composition which may fly off from matches which ignite at a lower temperature. The apparatus is heated by a regulated rose-burner.

Another form of apparatus consists of a glass vessel with a copper lid, in which four springs are arranged for carrying test-tubes. The thermometer can be inserted in the centre of the lid. The vessel is filled to about one-third with pure liquid paraffin. A copper wire

[1] *Cf.* K. Fischer, *loc. cit.*

stirrer passes through the lid. The matches to be tested are hung on the ends of copper wires in the test-tubes.

This apparatus is similar to that described for explosives (*cf.* p. 554).

In testing sulphur matches and wax matches, the sulphur or wax should first be removed, as the wax in every test, and the sulphur when the temperature became too high, would melt, and enclose the match-head.

The determination of the ignition temperature can also be carried out by the method devised by Leyque and Champion. A copper rod, which is to be heated at one end, has at the other end indentations, 10 cm. apart; these concavities or holes are filled with oil or with d'Arcet's alloy (sometimes called Newton's alloy), consisting of 8 parts of bismuth, 5 parts of lead, and 3 parts of tin, and melting at 94·5°. The rod is provided with six holes, and has a length of about 70 cm. from the first hole. Thermometers are inserted in the holes, and that point on the rod is found at which the match composition will ignite. This method is less exact and more troublesome than that of Fischer.

The apparatus employed by Bein to determine the inflammability of gun-powder [1] can also be used.

Kostevitch [2] has described a glass apparatus suitable for the determination of the ignition point of explosives, and also the first signs of ignition of inflammable materials. For explosion point determinations a metal apparatus is employed in which Wood's alloy is used as the heating medium.

C. BEHAVIOUR UNDER PERCUSSION

K. Fischer [3] recommends a method by which the results can be expressed in figures. He uses a striking apparatus, consisting of an oak block, partly filled with lead, and protected beneath by an iron plate; this runs in two iron grooves, from a height that can be varied, and falls on to an iron plate on which the match is placed. The height of fall, multiplied by the weight of the block, gives the force necessary to ignite the match in kilogram-metres. The height of fall is 1 metre; the weight of the block can be increased as desired by addition of lead. The greatest weight of the block is 1·5 kg., so that the largest amount of work which the machine can do is 1·5 kg.-metres. The results are not very accurate, as several circumstances, friction, for example, are not taken into account. However, as these errors are the same in each test, the results are comparative. The sensitiveness of one and the same class of matches under percussion varies very widely. Matches

[1] Bujard, *Leitfaden der Pyrotechnik*, Stuttgart, 1899, p. 136.
[2] *Z. Ges. Schiess- u. Sprengstoffw.*, 1928, **23**, 156.
[3] *Arbeiten aus dem Kaiserlichen Gesundheitsamt*, vol. xix.

of the same class with large heads ignite more readily than those with small heads. In general, the scraped-off composition is more easily ignited than the match, so that in forming conclusions from this test as much care must be exercised as in judging the temperature of ignition. For a general review of the influence of shock on explosive materials see *Przemysl. Chem.*, 1936, **20**, 117; *Chem. Abstr.*, 1937, **31**, 2435.

D. SENSITIVENESS TO MOIST AIR

To test this property the matches are placed in a vessel over wet cotton wool, and the vessel then placed under a bell-jar over a vessel of water. Observations are made with regard to the behaviour of the matches when moist, their durability, appearance, stickiness, and the like.

E. BEHAVIOUR WHEN TREATED WITH CONCENTRATED SULPHURIC ACID BY MOISTENING OR BY IMMERSION

Observations are made as to whether inflammation of the match-head takes place with this treatment.

B. PRIMINGS AND FIREWORKS

Fireworks, so far as their active contents are concerned, are derived from a comparatively small number of components or mixtures (firework mixtures).

These comprise, on the one hand, easily combustible substances, such as charcoal, sulphur, antimony sulphide, resins, and tar ; and on the other hand, they include substances which readily give up oxygen and support combustion, such as saltpetre (potassium nitrate), and potassium chlorate or other chlorates. A third category includes those substances used for the various colour effects (barium, strontium, copper, and other salts), and also finely divided metals, and coarse particles of charcoal, to cause sparks and showers of fire (" golden rain," and the like). Other substances are sometimes used to decrease the rate of burning and to increase brilliance[1] (*e.g.* mercurous chloride and mercuric thiocyanate).

I. FIREWORK COMPOSITIONS

The following substances form the groundwork of most firework compositions :—Gun-powder (grain powder and meal powder), saltpetre and sulphur, charcoal mixture, and grey mixture.

[1] U.S. Pat. 1756255/1930.

A. GUN-POWDER

Ordinary coarse-grained gun-powder (grain powder) is used for impulsive or percussive charges (for throwing fireworks from bombs, mortars, etc.), or for explosions ; the coarse-grained powder is necessary in these cases as quick combustion and a rapid evolution of gas are required.

Further, meal powder, that is a finely powdered blasting powder, is used ; that employed by makers of fireworks is of varying composition. For instance, a blasting powder is used, which, powdered and passed through a 0·5 mm. mesh sieve, consists of :—

60·2 parts by weight of doubly refined potassium nitrate,
18·4 ,, ,, of sulphur,
21·4 ,, ,, of alder wood charcoal,

and explodes at 20° by Wagner's powder test.[1]

An ordinary blasting powder, consisting of 70 parts of saltpetre

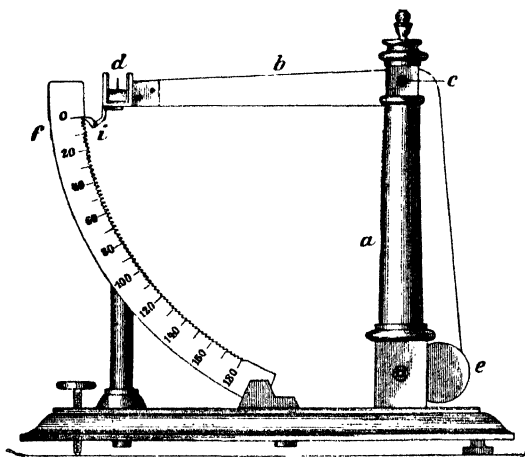



FIG. 128.

18 parts of sulphur, and 12 parts of charcoal is suitable. As a matter of fact, any ordinary gun-powder can be converted into meal powder, as its strength can easily be modified by the proportions of the ingredients. Meal powder is used when slow combustion is necessary. The qualitative and quantitative tests are carried out as detailed under Gun-powder (p. 517).

Wagner's Powder Test. In various factories, where fireworks are made, it is necessary, for some of the mixtures and for the calibre of the cartridges, to use a gun-powder of definite power. Tests by which the power can be estimated are carried out by means of Wagner's apparatus.

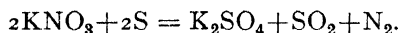
This apparatus (Fig. 128) consists of a column *a*, fastened to a

[1] *Cf.* Priker, *Kunstfeuerwerkerei*, 1892.

support, which can be levelled by means of screws; *b* is an angular lever, which moves on a hinge at *c*, and carries the counter-weight *e*. The unweighted arm *b* carries a small mortar *d* and a spring catch *i*, which moves over a graduated metal arc *f*. When the powder explodes, the arm is pressed downwards by the force of the explosion, and the distance through which it is displaced is shown by the spring catch. The number of degrees can be read directly from the graduated scale. The charge for each test is 2·2 g. of powder. The results obtained by this method are not very accurate, owing to the large size of the mortar, and the smallness of the charge; it is therefore necessary to repeat the test several times, and to take the mean of the results.

B. SALTPETRE AND SULPHUR

This is a mixture of 3 parts of nitre with 1 part of sulphur, and contains approximately equivalent weights of the two components. When this mixture, which yields very little gas, is burnt, the products formed are mainly potassium sulphate, sulphur dioxide, and nitrogen, in accordance with the following equation:—

$$2KNO_3+2S = K_2SO_4+SO_2+N_2.$$

This mixture is the basis for most compositions which are to give light, and also for grey mixture.

C. GREY MIXTURE

This is made by mixing 7 parts of meal powder with 100 parts of saltpetre and sulphur, and is mostly used for the manufacture of fire-balls (used in war).[1] These consist of twill bags, charged with compressed grey mixture, which is filled into them with the aid of spirit; they are fired by means of a composition fuse. Grey mixture mixed with antimony sulphide is used for torches.

This material can be tested in the same manner as gun-powder (p. 517).

D. CHARCOAL MIXTURE

This name is given to meal powder, of which 500 parts are mixed with 6 to 8 parts of charcoal. To this class also belong the slow mixtures or slow fires, which consist of meal powder, the explosion of which is more or less retarded by additions of charcoal. Further, there are quick and slow squib mixtures, also so-called "green" mixtures, which are made up of various kinds of slow mixtures. The green mixtures contain larger proportions of sulphur. In addition there are propelling mixtures, which consist of meal powder, nitre, and charcoal (sometimes a little chlorate of potash), and spark mixtures, similar to

[1] *Cf.* Bujard, *Leitfaden der Pyrotechnik.*, 1899, p. 16.

the last, consisting of nitre, sulphur, and charcoal. The former are used for war rockets, and the latter for firework rockets. It is necessary that these mixtures should evolve large quantities of gas, and they are therefore made with a meal powder to which charcoal has been added. An old Prussian prescription for war rockets is as follows [1]: 32 parts of nitre, 12 parts of sulphur, 32 parts of meal powder, and 16 parts of well-powdered charcoal.

Hence it is apparent that the charcoal mixture can be used, as these are very similar to the spark mixtures which consist of :—

Nitre	12 or 16 parts
Sulphur	3 or 4 ,,
Charcoal (coarse)	5 or 9 ,,

Spark mixtures are used for cases, constricted at one end, which can be suitably grouped and mounted, so as to be used for cascades of fire, suns, fans, palm trees, fixed stars, and various other kinds of fireworks. These mixtures are also made up with additions giving a reddish light, and with metal filings; those containing metals are known as "brilliant mixtures."

Finely divided metals, such as aluminium or magnesium, with various oxygen-containing substances, may be used for flashlights. Krebs [2] uses zirconium with the nitrate and barium nitrate or other oxidant.

Such mixtures are analysed similarly to gun-powder. For tests for potassium chlorate, see Vol. I., p. 618, and for the examination of the various ingredients, nitre, charcoal, and sulphur, see pp. 1, 7, 8. The same points must be noted in judging these substances as in match mixtures.

The determination of aluminium in flares or dust may be carried out by the method of Faber and Stoddard [3] by estimating the reducing power on litharge. The accuracy depends on the formation of a liquid slag from which the globules of lead can easily separate and on the temperature at which the assay is carried out. 3 g. of aluminium is mixed with 100 g. of litharge and 30 g. of borax glass and a cover of 25 g. of borax glass added. The fusion takes 20 minutes in a gas muffle.

E. ILLUMINATION AND COLOURED FIRE MIXTURES

In addition to the substances already mentioned, these almost invariably contain potassium chlorate, together with substances, such as strontium, for producing the colours. Strontium salts give a red colour, barium salts a green colour, copper salts blue, and sodium

[1] *Cf.* Busch-Hoffmann, Bolley's *Handbuch d. chem. Technik.*, vol. vi., p. 384.

[2] B.P. 352118/1930.

[3] *Ind. Eng. Chem.*, 1920, **12**, 576.

salts (*e.g.* oxalate and carbonate) a yellow colour. For extra brightness, magnesium powder is added. They are accordingly mixtures of combustible substances with compounds which give coloured flames, and like exploding gun-powder, they throw off small particles which continue to burn while in motion, and owe their power of projection to the combustion. At first sight, it would appear easy to make one of these mixtures, but several factors have to be taken into account, such as the velocity of combustion, which in the case of "stars" should be great, for coloured lights slower, and for flames slowest of all; the temperature at which the substance imparting colour will act best; the formation of slags, and their fusibility. To find out whether these substances are suitable for colour mixtures, they should be thrown in the form of a dry and very fine powder into flames of varying temperatures such as hydrogen flames, the temperature of which has either been raised by oxygen, or lowered with nitrogen, so as to find out the effect of different temperatures. But this test is not always successful; for instance, lithium salts impart an intense carmine coloration to flame, but do not produce a colour of anything like the same intensity in mixtures. The manufacturer mostly tests this by making a small sample mixture, consisting of:—

Potassium chlorate	20 parts
Sulphur	5 ,,
Gum mastic	1 part

If the substance to be tested gives a good fire coloration with this mixture, it can probably be used.

The following formulæ have been found upon actual trial to yield satisfactory green and red colour mixtures respectively (E. G. Clayton):—

	Green.	Red.
Barium nitrate	60	...
Strontium nitrate	...	63
Potassium chlorate	15	18
Sulphur	13	13
Realgar	11	...
Shellac	...	5
Charcoal	1	1
	100	100

Another green mixture is: barium chloride, 69 parts; lactose, 30 parts; shellac, 1 part. For a yellow light, a mixture of sodium nitrate, 20 parts; sulphur, 20 parts; antimony sulphide, 8 parts; and carbon, 2 parts, may be used. A mixture of powdered pitch, glue, and borax [1] will give an intense yellow flame.

[1] Ger. Pat. 443901/1906.

By mixing together combustible compositions, which give different colours, a tint is obtained, which is nearer to a white than to a mixture of the two colours. On mixing red and yellow a pale orange results; blue and yellow give a not very intense pale green; blue and red give violet, and this is the only good colour obtained by mixing; red and green give white.

For spark compositions the following can be used: nitre, sulphur, mealed gun-powder, charcoal, steel and other metal borings, aluminium, magnesium and various alloys, orpiment and antimony sulphide.

A number of phosphorescent light mixtures have been described by L. Vanino.[1] The constituents are heated together for 1 hour, the number of parts being in parentheses:—*Violet-blue*: quicklime (15·0), strontium hydroxide (5·0), sulphur (8·0), magnesia (1·0), sodium carbonate (3·0), lithium sulphate (1·0), and 6 ml. of 0·3 per cent. aqueous colloidal bismuth solution; or, alternatively, quicklime (17·0), strontium hydroxide (5·0), sulphur (8·0), lithium fluoride (1·0), magnesia (1·0), 1·0 ml. of 1 per cent. rubidium nitrate solution, and 6 ml. of 0·3 per cent. colloidal bismuth solution. *Violet*: quicklime (20·0), barium hydroxide (10·0), sulphur (9·0), sodium sulphate (1·0), potassium sulphate (1·0), lithium sulphate (1·5), 2 ml. of 0·5 per cent. alcoholic bismuth nitrate solution, 1 ml. of 0·5 per cent. aqueous thallium sulphate solution, and 0·5 ml. of 0·5 per cent. aqueous thorium sulphate solution (the nitrates may be substituted for thallium and thorium sulphates). *Blue*: strontium hydroxide (15·0), quicklime (5·0), sulphur (8·0), magnesia (1·0), sodium carbonate (3·0), lithium sulphate (1·0), and 6 ml. of 0·3 per cent. colloidal bismuth solution. *Green*: strontium hydroxide (20·0), sulphur (8·0), magnesia (1·0), sodium carbonate (3·0), lithium sulphate (1·0), and 6 ml. of 0·3 per cent. colloidal bismuth solution.

Among non-chlorate colour compositions, in addition to these already mentioned, are some containing borax.

Smokeless flash powders have also been described containing up to 28 per cent. of zirconium, zirconium hydroxide and magnesium, barium nitrate, barium oxide and rice starch.

The presence of sodium compounds in certain flame pyrotechnics is to be avoided on account of the masking influence of the sodium flame and also on account of the hygroscopic nature of sodium nitrate which might interfere with the proper functioning of the pyrotechnic. The sodium can be estimated by the method of Ball.[2] When a mixture of potassium nitrate, bismuth nitrate and cæsium nitrate in nitric acid is added to a dilute solution of sodium nitrate, even in presence of large amounts of potassium salts, the sodium is precipitated

[1] *J. prakt. Chem.*, 1930 (ii.), **127**, 16-19; *Brit. Chem. Abs.*, B, 1930, 841.
[2] *J. Chem. Soc.*, 1909, **97**, 2126; 1910, **99**, 1408.

quantitatively in a crystalline form as cæsium sodium bismuth nitrite ($5Bi(NO_2)_3 . 9CsNO_2 . 6NaNO_2$). The results are not very accurate. An improved technique has been described by Faber and Stoddard.[1]

F. POTASSIUM CHLORATE AND SULPHUR

This consists of a mixture, used for adding to illumination mixtures, of 125 parts of potassium chlorate and 35 parts of sulphur. The use of chlorates is restricted in mixtures on account of their sensitiveness and has been made illegal in some countries.

G. "COLD" AND "WARM" MIXTURES

If the components are simply mixed together, the mixtures are known as "cold" mixtures. "Warm" mixtures are those made by fusing the substances together. The following is a "warm" mixture:—Grey mixture, 85 parts; meal powder, 29 parts; and antimony sulphide, 5 parts. This is used for fire balls and for white fire. Bengal lights are also often made by fusion.

H. IGNITION MIXTURES

These are for the purpose of firing inflammable objects at a distance. They must be made in such a manner as to combine the property of burning slowly with the development of as high a temperature as possible. The mixture used in Prussia for this purpose consisted of 76 parts of grey mixture and 24 parts of colophony. In Bavaria a combination of meal powder with "warm" mixture was customary.

I. MIXTURES FOR SPECIAL FIREWORKS

The following mixtures are used. For fuses, a mixture of meal powder, charcoal, and mica; for "golden rain," meal powder, charcoal, and iron filings; for "silver rain," lead nitrate, potassium nitrate, and charcoal; for "comets" a little meal powder and charcoal. Picric acid mixtures were introduced by Dessignolle and Castelaz,[2] by Brugère,[3] and by E. Jacobsen, for causing detonations with coloured fires. With copper powder, green sparks are obtained; with magnesium, white; and with zinc, bluish-white.

The first named used ammonium picrate together with barium nitrate, strontium nitrate, etc.; the last used the picrates of strontium and barium, which, however, have to be fired by means of a fuse. These mixtures are best made by the manufacturer himself from picric

[1] *Ind. Eng. Chem.*, 1920, **12**, 576.
[2] G. Schultz, *Steinkohlenteer*, p. 456.
[3] *Zeit. f. Chem.*, 1869, p. 667.

acid and the respective carbonates. For the testing of picric acid, see p. 532.

A mixture of calcium nitrate and carbonate, potassium nitrate, magnesium or aluminium red lead and calcium resinate may be used as a tracer mixture.[1]

Whistling squibs are made with magnesium picrate. The mixture is prepared according to the formula of the inventor, Weiffenbach, of Stuttgart. 200 grams of picric acid and 800 g. of nitre are dissolved in hot water, and saturated with 30 g. of magnesium carbonate, and the precipitated crystals then dried.

Hexamethylenetetramine may be substituted for charcoal, shellac, dextrin, or sugar in pyrotechnics, especially in fireworks for indoor display.[2] Charred woodmeal or sawdust may also be used.[3]

A typical smoke composition is as follows: tetrachlorethane or chloronaphthalene, 40 to 50 per cent.; zinc filings, 35 per cent.; nitre saltpetre, pitch and calcium silicate, 15 per cent.

As an example of a detonating firework composition the following may be given [4]: phosphorus sulphide is mixed with an oxidant and an inorganic binder consisting of magnesium oxide and an alum.

J. MERCURY FULMINATE[5]

This is used for percussion caps, either alone, or mixed with other combustible substances, or with gun-powder, potassium chlorate, nitre and sulphur, etc. These additions serve the purpose of retarding the decomposition, and of increasing the volume of the gases formed. Percussion caps are made of thin rolled copper sheet. The following is a prescription for this mixture:—100 parts of mercury fulminate are rubbed into a paste with 30 parts of water on marble slabs with boxwood rubbers; to this are added 50 parts of nitre, or 62·5 parts of nitre and 29 parts of sulphur. The paste is dried on sheets of paper, and granulated by means of hair sieves. Some makers, after placing the grain in the percussion cap, cover it with a small copper plate, while others coat the grain with mastic varnish. Discs of varnished tinfoil, or paper, or of both together, are sometimes used. 1 kilogram of mercury after conversion into the fulminate is sufficient for 40,000 percussion caps.

Analysis of Mixtures containing Mercury Fulminate. F. W. Jones and F. A. Wilcox [6] advise, in a mixture containing potassium chlorate, the fulminate, and antimony sulphide, first to extract the fulminate

[1] U.S. Pat. 1593721/1926. [2] Brock, B.P. 152529/1919.
[3] *Ibid.*, 304356/1916. [4] U.S. Pat. 1712555/1929.
[5] For the more specialised use of mercury fulminate in initiators, see p. 547.
[6] *Chem. News*, 1896, **74**, 283.

of mercury from a weighed quantity by means of a solution of ammonia in acetone, then the chlorate with water, and to weigh the residual antimony sulphide.

Chlorates are usually determined by conversion to chlorides by a suitable reducing agent and estimation as silver chloride ; or by heating with excess of conc. hydrochloric acid, when the gases evolved set free an amount of iodine (estimate with thiosulphate) from potassium iodide equivalent to the weight of chlorine present in the gases evolved. For the presence of potassium perchlorate in ammonium nitrate and chlorate mixtures the method of Bunge [1] may be employed : 100 ml. of an aqueous extract of the explosive is mixed with 20 to 25 g. of powdered quartz, the mixture is evaporated to dryness and ignited. Potassium is then determined in an aqueous extract of the ash by the perchlorate method, a correction being made for any potassium chloride or nitrate originally present in the explosive. For rapidly determining perchlorate alone in explosives containing only small amounts of other potassium salts and nitroglycerin, 5 g. of the explosive is mixed with 20 g. of powdered quartz, and the mixture is heated in a quartz crucible. The ammonium salts are thus decomposed, and the aqueous extract of the ash is analysed as before.

H. Brownsdon [2] estimates the mercury fulminate by decomposing it with excess of sodium thiosulphate, and determining the resulting alkalinity by $N/10$ sulphuric acid, previously standardized against pure fulminate.

The method has been improved by Philip.[3] He dissolves the fulminate in a large excess of potassium iodide and a known volume of a standard solution of sodium thiosulphate is also added. The excess of thiosulphate is titrated with standard iodine solution after neutralization with standard acid.

Marqueyrol [4] extracts the mixture containing mercuric fulminate and other compounds with a 5 per cent. solution of potassium cyanide. The extracted mercury salt is electrolysed and the mercury estimated in the usual way.

The explosive properties of fulminate of mercury have been studied by Berthelot and Vieille, who give the following equation for its decomposition : $(CNO)_2Hg = Hg + 2CO + 2N$. When mixed with 30 per cent. of water, it can be rubbed on a marble slab, with a wooden rubber, or a soft, clean cork, without any danger.

The following are the results, in round numbers, of a series of analyses of several kinds of percussion caps, in one of which lead

[1] *Chem. Zeit.*, 1930, **54**, 915 ; *Brit. Chem. Abs.*, B, 1931, **50**, 6, 136.
[2] *Chem. News*, 1904, **79**, 302.
[3] *Z. ges. Schies- u. Sprengstoffw.*, 1912, **7**, 109.
[4] *Bull. Soc. Chim.*, 1920 (iv.), **27**, 448.

thiocyanate had been used instead of mercury fulminate (E. G. Clayton) :—

	1.	2.	3.	4.	5.
Mercury fulminate	33	21	25	27	...
Lead thiocyanate	...	...	...	...	36
Antimony sulphide	15	45	34	...	...
Sulphur	...	...	...	7	...
Ground glass	...	...	18	43	...
Potassium chlorate	52	34	23	23	64
	100	100	100	100	100

	G.	G.		G.	G.
Approximate weight of charge per cap	0·025	0·046	...	0·022	0·025

In these analyses, Brownsdon's method was employed for the determination of the fulminate, the antimony was estimated volumetrically, the lead gravimetrically, and the thiocyanic acid by a colorimetric method ; the figures for potassium chlorate were obtained by difference.

II. Detonators

Initiating explosives (detonators, including railway detonators) may be examined by mixing the detonator with varying amounts of an inert substance (*e.g.* talcum [1]) until a number of cartridges of a mixture do not detonate regularly when fired with the detonator under examination. The two ingredients used in the test are picric acid and olive oil. The strength of the detonator may also be measured quantitatively by the Wohler test.[1] The initiating effect on 2 g. of trotyl (trinitrotoluene) or troxyl (trinitroxylene) mixed with paraffin is measured. Equal weights of the explosive (*i.e.* trinitrotoluene) are mixed with a standard paraffin oil to give a series of samples with varying paraffin-oil content. The explosion is carried out with 2 g. of each grade of trotyl in a copper tube of 10 mm. diameter placed on a plate 5 mm. thick. The maximum percentage of paraffin oil which still allows complete detonation is taken as a measure of the strength of the detonator.

III. Primings

A. The Firing-Exciter

This consists of a mixture of meal powder and alcohol. A fast exciter consists of 1000 g. of meal powder and 570 ml. of alcohol ; a

[1] *Z. ges. Schiess- u. Sprengstoffw.*, 1930, **25**, 393.
[2] *Ibid.*, 1925, **20**, 145, 165 ; 1926, **21**, 1, 35, 55, 97, 121.

slow exciter of 1000 g. of meal powder and 720 ml. of alcohol. These mixtures are best made with the hands in a copper pot, or in a porcelain basin. The exciter is painted on to the quick match at the firing hole, where the paper of the covering of the firework has been twisted together, for instance where the fuse is fastened to crackers and squibs. In general all those places which are intended to catch fire are painted with this mixture. If it is intended to stick tightly, a solution of 16 g. of gum arabic in 140 ml. of water is added. The tests used are similar to those employed for gun-powder (p. 517).

B. SLOW AND QUICK MATCHES, FUSES

Triple and quadruple cotton threads, purified from grease as for gun-cotton, are soaked in quick firing-exciter, and sprinkled with meal powder. After the impregnation they are allowed to lie for six to eight hours, then rolled on a bobbin and passed through a board, provided with holes of various sizes, so as to impart the required strength and uniform thickness to the threads after air drying. They are again passed through the firing-exciter, which has been thickened with gum arabic, then again through the holes in the board, sprinkled with meal powder and dried ; finally they are wrapped in paper, placed in dry boxes, and stored in a dry place. According to the formula used for the Prussian artillery, the following quantities are necessary for a fuse 100 metres long, and 0·52 cm. in diameter : 2·94 kg. of meal powder, 4·35 litres of alcohol, 21·2 g. of gum arabic, and 0·24 kg. of cotton thread. Thus prepared, the speed of burning is 1 metre in 24 secs.

Better fuses are obtained by a previous treatment of the cotton with a special mordant (cf. *infra*).

In the case of a *train of powder* (or *leader*) the fuse is covered. These covered fuses protect the firework against pre-ignition, and also cause a quicker firing. For this purpose the fuses are covered with paper tubes.

Quick Matches or *Paper Fuses* are made of cotton wick boiled in a solution of gum and mealed powder and partly dried. The wick is then dusted with mealed powder. It may be used in this form or enclosed in a tube, when it burns more rapidly (approximate rate : 1 foot in 1 to 3 secs.). As a rule, they are about 28 cm. long, and 0·33 to 0·21 cm. in diameter.

The Mordant for Fuses serves in the first place to make the fuse more inflammable, and secondly, to ensure a steady and quiet combustion, for instance, as in time fuses. The mordant consists of a solution of 1 part of nitre in 10 parts of water. The dry cotton threads are allowed to remain in this solution for twelve hours, and are then wrung out and dried.

Slow Matches as prepared for pocket match-boxes, are obtained by boiling loosely spun cotton in a solution of lead nitrate, consisting of 1 part of lead nitrate in 10 parts of water or in potassium nitrate; they are then allowed to dry in the air without being wrung out. Another method consists in boiling the cotton in a solution of lead acetate (1 part of lead acetate in 20 parts of water) and when dry, placing them in a solution of 1 part of potassium bichromate in 10 parts of water. The threads so made are yellow, owing to the formation of lead chromate. This fuse smoulders at the rate of about 1 foot in 3 hours, and used when a long delay is required.

In the Sheune[1] fuse lead tubing is filled with powdered trinitrotoluene. The explosive is melted and drawn into the tube by suction, and when cold the tube is drawn out to a diameter of 4 mm. The tube may also be filled with molten trinitrotoluene and allowed to cool.[2] The length is increased by hammering. The temperature of the explosive is kept below its melting point during the treatment and a current of air directed on the tube. In this way a more sensitive *cordeau* or fuse is obtained.

Electric fuses are also used.[3]

Fuse Paper. In dry weather this can be used in place of the ordinary fuses, and finds general use for certain firings. It is made by spreading firing-exciter on to both sides of sheets of blotting-paper, sprinkling it with meal powder and drying it.

C. GUN-COTTON FUSES

The preparation of gun-cotton fuses is exactly the same as that of gun-cotton. They can be tested as described in the section on Nitrocellulose (p. 520). These fuses transmit fire faster than any other form, and are mostly used for firing large set-pieces; they burn very fast, and will fire a fuse-paper wrapped round them with absolute certainty; they have the further advantage that they can be used in wet weather.

D. PORT-FIRES

These are fireworks which will cause the firing of charges and of other fireworks quickly and safely in cases where the fuse cannot be used. Port-fires must therefore be capable of burning very well, and must not be put out by even the strongest shower of rain. The mixtures employed must be very rich in oxygen, and it is recommended to fuse together the nitre and sulphur mixture used in their manufacture.

[1] *Annales des Mines*, 1907; *Z. ges. Schiess- und Sprengstoffw.*, 1908, 141.
[2] U.S.A. Pat. 1741380/1929.
[3] *Annales des Mines*, 1908, 361; 1909, 41; 1911, 352; 1912, 459.

Port-fires are about 40 to 50 cm. long, and should give a flame 8 mm. long. The necessary casing is made of strong cardboard, and is soaked in a solution of nitre so that it should burn easily; the diameter is about 1 cm. The mixture is filled into these cases, about 5 cm. deep at a time, and slightly compressed: sometimes it is moistened with linseed oil. The composition of some typical port-fires is as follows:—

	Swedish Mixture.	French Mixture.	Prussian Mixture.
Nitre	24 parts	6 parts	100 parts
Sulphur	14 ,,	3 ,,	100 ,,
Meal powder	11 ,,	1 part	85 ,,
Colophony	1 part	...	7 ,,

E. COMPOSITION FUSES

These are really only port-fires on a smaller scale; they are fastened to fireworks and effect a certainty of firing. They are made of strong paper, have a diameter of 0·5 cm. and a length of from 6 to 8 cm. They are filled up to 2 to 3 cm. with meal powder, on the top of which a layer of priming-mixture is placed. Such mixtures consist of: Nitre and sulphur, 100 parts; meal powder, 25 parts. The mixtures used for time fuses can also be employed.

F. TIME FUSES

Many fireworks (set pieces) can only be successful and produce the desired effect if some parts, such as torches, squibs, etc., have a definite time for burning. Time fuses are used for exploding charges, or for igniting fireworks in a definite period of time. These time fuses are tubes filled with a mixture in such a manner that a certain length will burn in a definite time.

As in the case of igniters, the differences in the action of time fuses are based solely on the proportions of a few constituents (powder, nitre, sulphur, etc.), and upon the density of the mixtures. Their examination is conducted as described above. The main requirement in the case of these fuses is to determine the time of burning.

IV. The Duration of Burning

In fireworks, the maintenance of a definite duration of burning is especially necessary where set pieces are used, or where rotations are required and the like. It is less necessary in the case of rockets, when they are to be let off together in the form of a fan, etc., or in a quantity of squibs, because the composition and compression of the

mixtures used are sufficient to regulate the combustion. The duration of burning of a mixture is dependent upon :—

1. The composition.
2. The degree of dryness.
3. The degree of fineness, and the thoroughness of mixing.
4. The degree of compression.
5. The area of its burning surface.
6. The area of the delivery opening.
7. The nature of the covering.

From this it is obvious that successful results can only be obtained by working with uniformly made mixtures, with the same covering material, and uniform charging. Small divergences nevertheless occur, but these can be neglected, as they make no difference, when the firework is ignited. Moisture in the mixture retards the firing, not only directly by its presence, but also because it causes reaction, mainly between the sulphur and the metals in the mixture, when the fireworks are stored. The area of the delivery opening retards the firing when it is less than $\frac{1}{5}$ to $\frac{1}{6}$ of the area of the case.

The duration of burning is determined with a stop-watch, and is of importance in the case of set pieces, in which several kinds of mixtures are present. The time can then be regulated by altering the depth of the mixture in the cases ; shorter cases for slower mixtures, and longer cases for quicker mixtures, can be used.

V. Testing Firework Mixtures for Liability to Spontaneous Combustion

Some compositions used in the manufacture of fireworks have pyrophoric properties ; for example, mixtures containing iron filings and sulphur, which have become damp ; also certain Bengal light mixtures. Illumination mixtures containing nitrate of strontium or barium, sulphur and potassium chlorate, will often fire of their own accord, after standing for a few hours. This occurs chiefly when the ingredients have been quickly dried before use, and when the mixture is left lying in a warm, moist place. An ignition of this nature can be prevented by making the mixture of pure materials. A better preventive, according to Clarke, is an addition of a small quantity of antimony sulphide, or of a small quantity of sodium carbonate or chalk, as in the case of nitrocelluloses. The latter take up any acid impurities of the sulphur or other components, and form compounds which are inactive with chlorates and nitrates. This treatment is of some use, but the action of antimony sulphide is questionable. Mixtures

which have become damp, must be dried separately and with great care, as they ignite easily. Mixtures containing copper oxide also fire readily, but this can be prevented by substituting copper carbonate for the oxide. Traces of permanganate or bromate are also dangerous.

The test proposed by Meischmeier is carried out as follows: 5 grams of the mixture is slowly heated in a dish on a sand-bath, to 100°, and kept at this temperature for two hours. If it is now moistened with water, and again dried, it should not ignite spontaneously.

TEXTILES AND TEXTILE CHEMISTRY

THIS section includes the physical and chemical tests of textile fibres and fabrics ; the tests for dyestuffs used on textiles and for the auxiliaries and detergents employed in their treatment ; in conclusion, tests for finishes and their defects are given. The whole section has been prepared under the general direction of J. M. Preston, B.Sc., A.I.C., of the Textile Chemistry Department, College of Technology, Manchester, with the aid of various collaborators.

TEXTILE TESTING

By J. M. PRESTON, B.Sc., A.I.C., College of Technology, Manchester

I. TEXTILE MICROSCOPY

THE microscope is often most useful in conjunction with other methods of investigating textile problems. In applying the instrument, two features must not be overlooked: first, the necessity for training and experience in microscopical observation, and secondly, the question of sampling. Fortunately, absolute values are not often needed and more frequently comparison of normal and abnormal fibres is required.

The two branches of textile microscopy to be considered here are the analysis of faults and the assessment of quality. Identical methods are often used for both these purposes, though for the former they tend to be more qualitative and for the latter more quantitative.

In general, microscopical examinations can be divided into those made at low and those made at high magnifications. The former are used in the investigation of the structures of yarns and fabrics, and the latter in the investigation of the appearance and properties of fibres.

A. FABRICS

Fabric structures are most conveniently examined by means of low-power binocular magnifiers, which are fitted with erecting prisms so that the image is seen the right way up and right way about. These magnifiers have a large field of view, which is essential, since peculiarities of structure disappear unless there is, for comparison, a large background of normal structure which can be seen at the same time. Magnifications of 5 to 10 times are the most useful, since with higher magnifications the field is generally too limited in area. Useful results can also be obtained by an ordinary monocular microscope if an objective of 1½ to 3 ins. focal length is used together with a low-power eye-piece. This arrangement, however, has the disadvantages that the image is inverted and reversed, making manipulation difficult, and that the image is flat instead of having the solidity and depth of the images formed by the binocular instrument.

Illumination of Fabric Surfaces

The method of illuminating the fabric is even more important than the instrument used for the examination. To get good results the illuminating arrangement must be very flexible, it must be possible to throw uniform lighting downwards at angles from those of grazing incidence to those as nearly vertical as can be arranged without fouling the microscope. Further, it should be possible to vary the azimuth of the lighting so that it comes from one side only or from all sides at once.

Several different methods have been used to illuminate specimens for examination by reflected light. The best one is an arrangement of a number of lamps set in a circle surrounding the observing lens. The frame holding the lamps can be moved nearer or farther from the specimen and the lamps are provided with individual controls, so that any illumination from a single lamp to the whole ring can be used.[1] Failing a special arrangement of this kind, quite a good makeshift arrangement is possible with two or three lamps on separate stands and a few white cardboard reflectors.

Whatever method of illumination is used the important considerations are :—

(1) When colour differences are of interest, the light should be diffuse (or from a large source) and fall on the specimen from as nearly as possible the direction of the observing lens.
(2) When the structure of the specimen is of interest, the light should be from a small source and fall at a comparatively small angle to the plane of the specimen.
(3) When structures projecting from the surface of the specimen are of interest, the light should fall on the specimen so that it only just grazes the surface.

These directions for arranging the lighting must be taken as a general guide only. The optimum conditions in each particular case are different and, generally, time spent in experiments with the lighting to find the best method is amply repaid in the quality of the results. This is specially marked in photomicrography, where striking results must be obtained if they are to carry conviction.

Preparation of the Fabric

The fabric must be mounted on a firm flat surface such as a sheet of glass. It must lie flat. If it is creased, it is preferable to flatten it by ironing, rather than by stretching over the support, since it is very difficult to stretch it evenly, and uneven stretching deforms the

[1] Preston, *J. Roy. Mic. Soc.*, 1931, **51**, 115.

structure. At this stage some consideration must be given to the background placed below the fabric. When colour variations are being looked for it is valuable to place a piece of white paper under the fabric. This reflects light through the gaps in the structure and thereby gives a more uniform field in which to search for colour variations. When, however, the only interest lies in the surface structure, a piece of black paper should be placed below the fabric.

Examinations by Transmitted Light

When examining fabrics for both colour and surface structure variations, the fabric should be viewed by reflected light as just described. When, however, the interest lies in the internal structure, it is better to view the fabric by transmitted light. If the fabric mounted on a sheet of glass is examined, it will look rather like a piece of wire gauze. No fine details will be visible. To obtain good results and to make the details visible, the fabric must be placed in a shallow glass cell. A liquid mountant is run into the cell so as barely to cover the fabric, and a piece of thick plate glass lowered slowly on to the fabric. Care should be taken to avoid trapping air bubbles. The fabric is now ready for examination.[1]

Illumination for Low Powers. Prepared as described above, the fabric is in effect equivalent to a negative that is to be enlarged. The optical system used for illuminating the fabric is the same as that of a photographic enlarger. In fact an ordinary enlarger can conveniently be used for projecting an enlarged image on a screen. If an enlarger is not available, or for some other reason not desirable, then an equivalent optical system must be arranged for illuminating the specimen. The light must be passed through either a condenser or a diffuser before reaching the fabric. Flashed opal glass is the best diffuser, but the illumination from a condenser is very much brighter.

Mountants.—The use of a liquid mountant gives another means of control which is absent when the specimen is dry—by the choice of a liquid with a suitable refractive index it is possible to accentuate some features at the expense of others.[2] Thus, when the refractive indices of both the fibres in the fabric and the liquid are the same, the fibres will disappear unless they are dyed. Any variation in colour can then be seen very clearly. In addition, foreign bodies of which the refractive indices are different from that of the liquid, will show up clearly. Thus, delustred viscose rayon containing particles of TiO_2 will appear opaque because of the presence of these particles and similarly other fabrics with other foreign substances.

[1] Lassé, *Textilber.*, 1931, **12**, 249. [2] Mullin, *Acetate Silk and its Dyes*, London, 1928.

If the fabric is composed of more than one kind of fibre, and if these fibres have different refractive indices, as many different kinds of fibres have, by the choice of suitable liquids, one or other of these fibres can be made to disappear at will.[1] As general mountants in which all fibres are transparent enough for details to be seen but do not disappear, water, alcohol, and light petroleum are most useful. The table below contains a list of those mountants which make the different groups of fibres as transparent and invisible as possible.

Fibres.	Mountant.	Refractive Index.
Silk and native cellulose . .	Brombenzene or anethole	1·560
Wool	*o*-dichlorbenzene	1·550
Regenerated cellulose rayons .	Methyl salicylate	1·538
Acetate rayon . . .	Limonene or medicinal paraffin	1·473

Colour Filters. When a coloured fabric is examined, colour filters may be used either to accentuate the colour or to render it less obtrusive. For the former effect a filter of a contrasting colour is used, for the latter a filter of the same colour as that of the fabric. No ordinary colour filter will reduce the obtrusiveness of the colouring of very darkly dyed fabrics, but as most dyes are transparent in the infra red, an infra-red filter can be used with advantage, for photography and, if the light is bright, for visual observations as well. Of course, when making observations using infra-red light, extraneous visible light must be carefully excluded.[2]

Applications. The methods of low-power microscopy prove useful in detecting many defects in fabrics. Examples are : the examination of printed designs, when these show imperfections ; the examination of stains ; the examination of dirty and defective yarns in fabrics, without dissecting the fabric ; the examination of defective fabric structures, such as tight picks or ends, reediness, " cracks," variations in yarn spacing and crepeing ; examinations for the presence of foreign bodies, such as cotton-seed coats ; the examination of worn fabrics, or such as have been subjected to abrasion either in the form of yarn or fabric, where dissecting the yarn out of the fabric would mean losing the spatial relation of the fault in the yarn to the fabric structure.

[1] Preston, *Modern Textile Microscopy*, p. 41, London, 1933.
[2] Preston, *Leica News*, 1937, 99.

Descriptions of the applications of microscopy to textile faults in general, which are illustrated by many beautiful photographs of fabrics, are contained in a series of articles by Herzog.[1] Reference should be made to these and to the series of illustrated articles on faults in rayon fabrics by the present writer.[2]

B. FIBRES

The low magnifications which are used for examining fabric structures are quite inadequate for fibres themselves. These are so small that they must be highly magnified to study their morphology. Otherwise a fibre approximates to the geometrical definition of a line and a fibre cross section to a geometrical point. The lowest useful magnification is about 50 times, whilst for the examination of intimate detail, a magnification of 1000 times is not too much. The magnification used must not be in excess of that for which the optical system is suitable, nor greater than the specimen can stand. Empty magnification must be avoided. The higher the magnification to be used the more care must be exercised in preparing the fibres for examination. Both slide and cover-glass must be scrupulously clean and the mountant must be free from dirt and air bubbles. To those with only slight microscopical experience, such minor details of technique as those just mentioned might appear unimportant, or if not that, at least that they are a matter of course. This is not so. Only when conscious attention is paid to each detail of technique will good results be obtained.

Mounting. Cross sections require a special technique for their preparation which will be discussed later, but unless they are prepared by the " plate method " (p. 656), once they are on the slide the mounting and subsequent treatment is similar. All fibres must be mounted, unless there is some special reason against this. The reason for this is a purely optical one. Mounting reduces glare, improves transparency and increases the resolving power. It enables fine structure and internal details to be seen which would be obscured by the heavy shadows in an unmounted specimen. The only occasion on which a fibre should be examined unmounted is when the surface of the fibre is the main interest.[3] Even then it is better to use a different technique, to examine a cast of the fibre in celluloid (p. 660).

Mountants. Occasionally fibres and sections are mounted in special media, such as sodium hydroxide solution or Schweizer's reagent, which produce the optical effects discussed above, but also have a swelling action. Generally, neutral mountants are used. These

[1] Herzog and Koch, *Textilber.*, 1937, **18**, 429, 505, 593, 701, 785, 869, 965.

[2] Preston, *Textile Manuf.*, 1936, **62**, May Sup., xlv.-xlvii., 212, 258, 302, 342, 382.

[3] Preston, *J. Soc. Dyers Col.*, 1930, **46**, 295.

may be either temporary or permanent. When making a large number of preparations for routine tests, the specimens generally have no permanent value, and it is better to use temporary mountants which can be removed easily, thus enabling the slides to be used again. A further argument in favour of temporary mountants is that one can be removed and another applied. In addition, temporary mountants can be obtained in a great range of refractive indices.

Permanent mountants are indicated if the specimen has to be kept for future reference. The best plan is to make a series of preparations in temporary mountants and to select the best and most characteristic, from which permanent mounts are then made. Other cases when permanent mountants are indicated are for photography when the fluidity of a temporary mountant might allow the specimen to move during an exposure, and, for a similar reason, when the microscope has to be used horizontally.

Apart from the factors of toxicity, volatility, and chemical action on the fibres, the main guiding principle in choosing a mountant is the suitability of its refractive index. If the interior structure is alone of interest, then the mountant must have the same refractive index as the fibre. Exact equality of refractive indices is hard to attain for two reasons. First, since they are anisotropic, all fibres have two indices with different values, and plane polarized light must be used if optical homogeneity is required. Secondly, there are slight differences between the refractive indices of the fibres in any sample. When a fibre is mounted in a medium of exactly the same refractive index as its own, the surface of the fibre disappears completely, unless outlined by foreign substances of different refractive indices. At the same time any foreign bodies inside the fibre are seen most clearly. This form of mounting is indicated particularly when using dark ground illumination and searching for minute foreign bodies in fibres. Since structure disappears it is also indicated when examining for stains by direct light. As temporary mountants when using unpolarized light those given in the table on p. 652 can be used. As permanent mountants the only two available are euparal, refractive index 1·50, and canada balsam 1·53.

For a general examination of the structure of fibres the mountant must have a refractive index different from that of the fibres. As temporary mountants water, alcohol, and light petroleum are suitable, though they are all rather volatile. As a permanent mountant, glycerine jelly is the only one suitable for all fibres, though it has the property, which is in certain cases a disadvantage, of swelling fibres in a similar manner to water. Euparal is suitable for all the fibres with higher refractive indices, but not for acetate rayon, which it renders too transparent.

Preparation of Fibres for Mounting

(a) *Entire Fibres.* For rough examinations it is sufficient to take a bundle of fibres which are rendered parallel by drawing between the fingers, or by combing with a fine metal comb. This bundle should consist as far as possible of a single layer of fibres. It is laid on the slide, covered with a cover-glass, and the temporary mounting liquid run in under the cover-glass from one side with a pipette. It is best to use excess of liquid, as this obviates air bubbles, and to remove the excess with a piece of filter paper touched against the edge of the cover-glass. The excess must be removed, otherwise, if the slide is tilted at all, the cover-glass will float off, away from the fibres. The fibres can then be examined.

For more important examinations and for photography a more elaborate technique is advisable. A line of adhesive is drawn across the slide on each side of the space which will be occupied by the cover-glass. The fibres are laid one by one parallel to the long edge of the slide, so that they are held at each end by the adhesive. They can then be mounted as described above. A suitable adhesive is one that sets by cooling—du Noyer's cement is admirable.[1] It is made by first melting some lanolin in a porcelain basin to dry it, and then stirring in resin while it is still hot. The mixture is heated and stirred till of uniform consistency. The ingredients are mixed in the following proportion :—

Lanolin	20 g.
Colophony resin	80 g.

The cement can be applied by means of a heated metal wire, which is dipped in the bottle of cement and then drawn across the slide leaving a trail of cement. As each fibre is laid over the cement on the slide it can be made to adhere by touching it with a hot wire.

When doing mercerization counts, it is convenient to have a large number of short lengths of fibres on the slide. The fibres can be obtained in this form by the following method : wind the mercerized yarn round an ordinary lead-pencil in a tight spiral and cut across the yarn with a pair of safety-razor blades. The blades should be clamped together by a pair of nuts and screws passed through the holes in them. The double-cutting edge formed in this way cuts off short lengths of fibres from the yarn. The short lengths are held between the blades, but fall out when the blades are separated and tapped on a slide. The short lengths of fibres are then teased apart by means of a pair of mounted needles. They are now ready for mounting as described above. Further details are given on p. 730.

(b) *Cross Sections.* The object of cutting cross sections of fibres is

[1] Du Noyer, *Compt. rend. Soc. Biol.*, 1918, **81**, 741.

to obtain information about their morphology that cannot be obtained from an examination of the entire fibres alone. In many cases the shape of the cross section is a valuable criterion of the nature and history of the fibre and gives information that either cannot be obtained or could only be obtained with difficulty in some other way. There are many methods of cutting cross sections of fibres, but there is no best method. Three of the better methods will be described, each of which is the best under the circumstances when it should be used.

For rapid diagnostic work where the highest accuracy is not required the plate method is indicated.[1] Without much practice, but with reasonable care, cross sections can be prepared in a few minutes with ease and certainty. An advantage of this method is that it requires only the very simplest apparatus. This is a metal plate about 0·5 mm. thick and the size and shape of an ordinary glass slide, bored through the centre with a hole 0·75 mm. diameter, some fine sewing cotton, and a safety-razor blade and holder such as is sold in the cheap stores. One or two additions are required in a few specially difficult cases, otherwise this equipment serves for all fibres. The technique is as follows: Take approximately a foot of the cotton, double this and pass the loop through the hole; now take the fibres which have been arranged parallel and select sufficient to just fill the hole; place these through the loop, and by pulling on the free ends of cotton draw the bundle of fibres into the hole (generally the bundle will be found either too large or too small, but a few fibres abstracted or added soon remedies this). If the fibres are hard, such as those of cotton or linen, they should now be thoroughly wetted. Soft fibres do not need wetting. The fibres are now ready for cutting. The razor blade should be laid flat on the slide which is supported on a firm surface, and tilted till the cutting edge is in contact with the surface. The projecting ends of the fibres are now cut off with a single slicing stroke. The slide is turned over and this procedure repeated. If the fibres were wet before cutting, the slide must be placed in a hot place to dry, otherwise this operation is not needed. The fibre sections are now ready for examination. The plate is placed on the microscope stage and the hole containing the fibre ends is covered with a cover-glass. Examination is preferably made with an 8 mm. objective and high-power eye-piece (10 to 20 times). Illumination should be from a condenser with the diaphragm stopped down and using light from a concentrated source.

The exceptional cases mentioned above are dark-coloured fibres in which a 0·75 mm. length would absorb most of the light, and raw cotton fibres where the convolutions scatter the light to such an extent

[1] Wollhof, *Rumstseide*, 1930, **12**, 316; Skinkle, *Amer. Dyestuff Rep.*, 1930, **19**, 362; Schwarz, *Textile World*, 18th Jan. and 15th Feb. 1930.

that the section outlines are indistinct. The dark coloured fibres should be entwined and intermixed with a large proportion of colourless rayon fibres before drawing into the plate. After cutting, a drop of the mountant which makes this particular rayon transparent (*cf.* the table on p. 652) should be run into the hole before covering with the cover-glass. A cover-glass should also be placed over the hole on the underside of the plate, where it will be retained by capillary action. The sections of the fibres now appear dark against a light background instead of the opposite as given by the normal technique.[1]

Raw cotton hairs should be smeared with a medium prepared by mixing together equal parts of melted glycerine jelly and liquid Indian ink (the mixture is evaporated on a water-bath till, on cooling, it sets to a stiff jelly). The medium is applied with a hot spatula to the cotton hairs after they have been placed in the loop of cotton but before being drawn into the plate. The bundle of cotton hairs is now drawn into the plate and more melted medium is gently squeezed into the projecting ends of the bundle. The plate is put on one side for the medium to set, after which it is cut in the usual way. Before placing on the stage for examination a cover-glass should be stuck on each side of the plate with a drop of glycerine. The sections will appear light against a dark background.

Sections cut by the plate method are only suitable for observations on their outlines. Although it is possible to see the lumens in raw cotton sections prepared as described above, fine internal structure cannot be observed. To prepare sections for observing this, other methods of section cutting must be used.

Beautiful sections of rayons, silk and wool can be prepared by the method of embedding in paraffin wax, and afterwards cutting in a microtome. This method is more laborious, slower, requires more apparatus, and a higher degree of manipulative skill than the plate method, but if these obstacles are overcome the results are much finer.

A small parallel bundle of fibres is taken and clamped at each end with a ¼-in. bull-dog paper clip. The bundle is placed in a metal mould, so that the bundle reaches to the bottom of each of the two slots and the clips hang down outside. The weight of the clips helps to hold the bundle straight. The mould is made of three pieces. Two L-shaped pieces of brass that fit together and form a rectangle which is supported on a slab of brass. These L-shaped moulds are available commercially, but they should have slots cut in them to half-way down each of the shorter sides. A mixture of 90 per cent. paraffin wax of melting point 60° with 10 per cent. beeswax is melted in a water-jacketed container (special water-jacketed vessels are sold for this purpose.[2] They should have lids to exclude dust when not in

[1] Preston, *J. Text. Inst.*, 1936, **27**, T, 216.

[2] For alternative wax mixtures see Barlow, *J. Text. Inst.*, 1938, **29**, T 111.

use.) The molten wax is poured into the mould containing the fibre bundle, and as the wax cools and contracts great care must be taken to keep filling up the mould with more molten wax. If this precaution is omitted the wax will set where it makes contact with the mould and will leave a hollow space in the centre, in which case the preparation is ruined. When the wax has set and cooled, the clips are removed, the components of the mould are separated, and the wax block removed, the fibre bundle will project from each of two opposite sides. A rectangular wooden block is taken in one hand and the wax block in the other. One of the faces of the wax block from which the fibres project and one of the faces of the wooden block are then warmed simultaneously over a small bunsen flame till the wax melts. The two hot surfaces are then pressed gently but firmly together, when they will adhere. The composite block is set aside to cool, and when quite cold the wax is trimmed away till the fibres project from the end of a square pyramid of wax. The small end of the pyramid should not exceed the size of a match-head. The block is now ready for cutting.[1]

Wax blocks are best cut in a mechanical microtome. There are several types of this instrument on the market, all of which are not equally satisfactory. The microtome should have a smooth and steady cutting movement, the thickness of the cut should be capable of being controlled to the nearest $2\,\mu$ and repetitive cuts should have exactly the same thicknesses; the razor used for cutting must be held firmly at both ends, and there must be arrangements for tilting the blade both in the plane of the cut and perpendicularly thereto and the degree of tilt must be capable of convenient control. The razor used should have flat sides and not be hollow-ground. The angle to which the cutting edge is ground should be increased by means of a sharpening back to 25° to 28°. It should have a facet at the edge which is smooth and ends in an unchipped cutting edge when viewed at 100-times magnification under the microscope. The facet should be flat and not rounded by stropping on a leather strop. Unless the cutting edge is perfect, inferior results will be obtained.[2]

The razor should be placed in the microtome holder and the back tilted upwards, so that the bottom side of the cutting facet is horizontal or slightly inclined downwards towards the edge. The razor should also be turned so that the edge makes an angle of approximately 60° to the direction of the cut. A suitable thickness of cut is $10\,\mu$, though thinner cuts are better with very fine fibres.

The wax block, prepared as described, is placed in the microtome and the wooden block is clamped in the holder provided. The fibres

[1] Preston, *Modern Textile Microscopy*, 1933, p. 56 *et seq.*
[2] *Ibid.*, p. 69 *et seq.*

must be perpendicular to the plane of the cut. The sections are now cut, and they should appear on the razor blade perfectly flat, or with only a very slight curl. If they curl badly the razor is not sufficiently sharp. The cuts should be made slowly otherwise the sections will be compressed. Under good conditions consecutive sections will adhere together to form a ribbon on the razor, which should be lifted up with a fine paint brush and placed (the same way up) on a prepared slide. The slide is prepared by smearing with a thin layer of Mayer's albumen.[1] This is made by mixing the following ingredients in the proportions stated :—

White of egg	50 ml.	Filter
Glycerol	50 ,,	
Sodium salicylate	1 g.	

A very small drop of this is applied to the slide and smeared into the thinnest possible layer with a clean finger. This fastens the cross-sections to the slide during the subsequent processes.

When several ribbons of sections have been put on the prepared slide, it is warmed over a small flame till the wax gradually softens and finally melts. The slide is then immediately dipped into a vessel of benzene or other wax solvent, removed, drained, placed in a vessel of alcohol, finally removed from this and allowed to dry in a warm place. The sections will now appear as white specks on the slide, but if excess of albumen was used the whole slide will be covered with a white film, and it will not be possible to see the sections by the naked eye. The slide should now be examined under a low power, and if the sections appear good, the preparation should be concluded by mounting it as described earlier.

The hard native cellulose fibres, as was stated at the beginning of this section, require a different technique. They are too hard to be cut when embedded in wax.[2] There are various methods of embedding them for section cutting, but only the gelatine method will be described. In this the parallel bundle of fibres held on a wire frame are immersed in alcohol for two or three minutes to drive out air, transferred to water, and then placed in a hot concentrated solution of gelatine, kept hot in a water-bath, for three hours. At the end of this period the fibres are removed from the gelatine and immersed in a mixture of 40 per cent. formaldehyde solution (5 ml.) and 95 per cent. alcohol (95 ml.) for several hours till hardened.[3] Finally the embedded fibres are immersed in absolute alcohol for a few minutes to harden, after which they are cut off the wire frame and treated as a plain fibre

[1] Mayer, *Internat. Journ. Anat. and Physiol.*, 1887, 4, 37.

[2] They can be cut in the wax mixture mentioned in the footnote on p. 657.

[3] Clegg and Harland, *J. Text. Inst.*, 1923, 14, T 489.

bundle and re-embedded in paraffin wax, as described above. They are cut in the microtome as described above, with the one difference that a razor with a more obtuse cutting angle is needed. The cutting facet should be sharpened to an angle of about 32° to 35°. Cross-sections which have been prepared by embedding in gelatin are generally mounted, leaving the gelatin *in situ.* In this case the best mountant is glycerine jelly.

(c) *Fibre Impressions.* In the case of opaque fibres, or of those which have a distinct internal structure, the observation of the surface morphology is confused. An example is the observation of the scales on a medullated animal fibre. Here the best method to adopt is to make a cast or impression of the fibre in a transparent medium and to examine this instead of the fibre.

One method is to place the hairs on a glass slide in a drop of a 1 per cent. solution of celluloid in amyl acetate, and then to cover them with a thin sheet of celluloid (Kodak's Kodaloid 0·003 in. thickness). The celluloid sheet should be held by light pressure to flatten the hairs and left to set overnight. After this the celluloid containing the hairs is peeled off the slide and the hairs pulled out. The impression in the celluloid sheet is now examined.[1]

Illumination for High Powers. To obtain satisfactory results not only must the fibres be properly prepared, but the optical system of the microscope also must be of good quality and properly adjusted. The light source should be of the concentrated type ; a " pointolite " enclosed tungsten arc lamp is the best all-round source, though for dark-ground illumination a clockwork feed carbon arc is better ; failing these, a low-voltage concentrated filament projection lamp is a fair substitute. The advantage of using a concentrated light source is that the image of the light source formed in the specimen can be varied in size to just fill the field of view and no more. This adjustment reduces glare to a minimum. The adjustment is made by the substage condenser and an auxiliary condenser fitted to the lamp. By varying the distance of the auxiliary condenser from the lamp a magnified, equal size, or diminished image can be produced, and this image is then treated as the light source and focussed on the specimen by the substage condenser. The advantage of the arc lamps over the filament lamps is that the actual radiating surface is more uniform, and can therefore be accurately focussed on the specimen. With a filament lamp the condensers must always be put slightly out of focus, otherwise the image of the filament will be seen and will confuse the picture. This increases glare and diminishes the quality of the final image seen through the microscope. Unfortunately the better the quality of the optical equipment the more the condensers must be put out of

[1] Manby, *J. Roy. Micr. Soc.*, 1933, **53**, 9.

focus. Contrariwise, little improvement will be found in using an arc lamp with inferior optical equipment. The average cheap microscope lamp, which is fitted with a diffusing screen of some kind, is only suitable for low-power observations.[1]

The auxiliary condenser should be of the aplanatic type and the substage condenser should be both aplanatic and achromatic. An oil immersion substage condenser is rarely of any use in textile work, and a good quality " dry " condenser with a maximum aperture of approximately 0·95 is more suitable. The condenser must be correctly centred in the substage, but centring screws scarcely justify themselves by their utility provided the objectives are properly centred in the nose-piece.

For low-power, dark-ground illumination a patch stop fitted just below the condenser is adequate, but for high-power observations a special dark-ground condenser will be required. The best type is one of the several variations of the cardiod condenser, in which the light undergoes two reflections in the condenser. This condenser must be fitted with centring screws, since it is far more sensitive to slight deviations from the optical axis than direct illumination condensers. An azimuth stop is a useful addition, which enables observations to be made on the shapes and arrangement of sub-microscopic structures, and is also useful with grosser structures.

The objectives should be of as good a quality as can be afforded, the apochromatic type is undoubtedly the best, but good achromatic ones are adequate for most purposes. The higher the power the more important is the quality of the objective. Thus, for example, better results can be obtained with a dry 4 mm. apochromat than with many oil immersion 2 mm. achromats, although superficially the higher numerical aperture (N.A.) of the latter would have suggested that the reverse would be true.

The minimum equipment would be a 16 mm. and a 4 mm. objective, but an 8 mm. is frequently very useful, while an oil immersion 2 mm. objective is necessary as a last resort when detail too fine for the other lenses must be studied. The last-named objective, though at times essential, is but infrequently used.

The objectives should be fitted to a revolving nose-piece, by which they can be quickly interchanged. A quadruple nose-piece is only a little more expensive than those taking fewer objectives, and is well worth having, since a battery of objectives can be kept ready mounted for immediate use, thereby saving both the time and trouble of interchanging objectives.

The eye-pieces should be of the type which suits the objectives in use—different ones are required for apochromatic and for achromatic

[1] Coles, *Critical Microscopy*, London, 1921.

objectives. Eye-pieces magnifying 5 times, 10 times, and 20 times are a suitable set. A micrometer eye-piece is a useful addition to the equipment. Since on occasions both lengths and areas must be measured, an eye-piece into which either a linear scale or a graticule can be fitted would be the best type, unless two micrometer eye-pieces are obtained.

A binocular microscope instead of a monocular instrument, while not a luxury, is not essential, but whichever is obtained it should be of large size and fitted with firm smooth adjustments. The stand should be fitted with a good mechanical stage, preferably of the rotating type, since this can be used for observations with polarized light.

A polarizer and an analyser should be available. Polarizing prisms are the best, but for most purposes the new " Polaroid " screens can be used with economy and very little loss in efficiency. They are also easier to adapt to an ordinary biological microscope stand, and on such a stand are in some ways preferable to polarizing prisms.

Choice of Mode of Illumination. Which of the several modes of illuminating the specimen is selected for use depends on the object of the examination. In general, the preliminary observations by which a conspectus is obtained should be made by direct illumination with the specimen mounted in a medium of different refractive index from itself. Similar illumination is used for the study of the external morphology of both entire fibres and sections at high magnifications. For the examination of coloured structures, where the colour or absence of it is of prime importance, the illumination should be similar except that the substage condenser diaphragm should be wider open, but the mountant should now have as nearly as possible the same refractive index as the specimen.

When searching for foreign bodies of a different refractive index from the fibres, or when looking for heterogeneity in the fibres or sections, dark-ground illumination and polarized light both prove essential.

As a means of assisting the identification of fibres or of examining their micellar structures, polarized light is often essential.

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II. QUALITATIVE TESTS OF TEXTILE FIBRES

Textile fibres can be classified by their chemical composition into four main groups—Mineral, Cellulose, Protein and Synthetic. The simplest test for rapid identification is the burning test, but this is not entirely reliable and must be confirmed by other tests, such as those given below and by a microscopical examination.

Mineral Fibres

Asbestos fibres are soft, pliable, and non-lustrous. They consist of magnesium silicate, with varying amounts of iron, calcium and sodium silicates. *Glass* fibres are lustrous and brittle.

Cellulose Fibres

These are carbohydrates, which may be almost chemically pure, as is bleached cotton, or encrusted with varying amounts of impurities, mainly organic in character, as in raw linen or hemp. Cotton and kapok are seed hairs which assist in the distribution of the seeds by air currents when ripe. Flax, jute, ramie, and hemp are bast fibres.

Rayons resemble the true vegetable fibres in their chemical properties. They consist of pure cellulose, which has been physically modified during the process of manufacture. They may contain some substances for delustring the yarn, the most usual at present being titanium oxide.

Esters and ethers of cellulose are made into yarns, but the only one made commercially on a large scale is cellulose acetate. In order to obtain solid effects when dyeing mixed fabrics and for printed goods, acetate rayons are partially saponified.

Synthetic Fibres

Various linear polymers of high molecular weight can be formed into fibres but at present only two—Nylon (polyamide) and Vinyon (polyvinyl chloride)—have been marketed.

Protein Fibres

These fibres differ chemically from the vegetable fibres in that they contain nitrogen and sometimes sulphur in addition to the carbon, oxygen, and hydrogen of the plant fibres.

Wool and Hair are cellular outgrowths from the hair follicles that are situated in the skin of all mammals. No hard-and-fast line

can be drawn between wool and hair. In general terms the hair fibre is more lustrous and stiffer than the typical wool fibre, and has not the same affinity for dyestuffs. Pure wool (and hair) fibres are formed of "keratin," and contain from 15 to 19 per cent. of nitrogen and from 2 to 4 per cent. of sulphur.

Silk is the product of a number of different tropical or semi-tropical caterpillars. As the grub approaches maturity, two large sacs in its body become filled with a viscous transparent liquid. When it is ready to enter into the next stage in its life-cycle, this liquid is extruded and at once hardens on coming into contact with the air to form a filament which may be a thousand yards or more in length. The silk ducts are situated on either side of the insect's mouth, and by appropriate movements the two filaments, which unite as they issue from the orifices, are woven into a protective cocoon, inside which the caterpillar turns into a pupa, from which later on will issue the perfect imago or winged moth. Directly the caterpillar ceases to spin, the pupa is killed by the application of live steam or dry heat. Subsequently the cocoon is softened in warm water, and the fibre reeled off. The dry "grege," as the silk is termed at this stage, still consists of one or more twin fibres, united by a coating of silk gum or sericin. On boiling in water or soap solution, the sericin goes into solution, leaving the pure silk fibres consisting of fibroin in the form of soft, single, glistening filaments. Fibroin contains nitrogen and resembles the wool fibre in its chemical composition, but contains no sulphur.

Silk is often loaded with mineral matter to give greater body and weight. The loading materials are present in the body of the fibres and cannot be removed by washing or simple extraction processes.

Fibres derived from casein to be used as a substitute for wool are being manufactured, though only on a small scale at present.

Filling Materials. In addition to the weighting which is given to real silk, low quality goods are often heavily loaded with starch, dextrine, china clay, Epsom salts and so forth. These materials adhere to the outside of the fibres and can be removed by simple extraction processes. Before testing textile fibres which are suspected to contain such filling agents, they should be extracted with hot water, dilute sodium carbonate solution, and dilute hydrochloric acid solution. An examination under the microscope is often of considerable assistance in deciding the presence of filling agents.

Oil. Yarns for some winding operations are heavily oiled, and before applying tests to them the oil should be removed by extraction with organic solvents.

Burning Test.—This is simply carried out by igniting a small portion of the fibres, allowing them to burn for a few moments and then blowing them out. The charred stump should be smelled, and

the odour (if any) noted, as this gives a valuable method of distinguishing the animal fibres. It should also be observed whether or not there is any ash or residue. In the case of weighted silk, the fibres will burn only with difficulty, and will leave behind a mineral skeleton which does not shrivel up as does the pure material. Mineral fibres will not burn, though glass fibres will melt.

The test can be refined by gently heating the fibres in a test-tube.

Vegetable fibres and acetate silk give off the smell of burning leaves, and the mixture of tarry and aqueous liquors condensing on the upper parts of the test-tube walls is acid to litmus.

Animal fibres give off a smell of burning feathers, and the distillate is alkaline, because the vapours evolved contain ammonia. Wool, in addition to the alkaline distillate, gives off sulphuretted hydrogen, which may be recognized by placing a cap of filter paper over the mouth of the test-tube, and a drop of lead acetate solution on the filter paper. The presence of sulphuretted hydrogen is indicated by a black or brown deposit of lead sulphide on the paper. Partly saponified acetate fibres will burn quickly like viscose if placed in a flame, but heated gently in a test-tube they will melt and form a black bead like normal acetate fibres.

Staple Test.—This test is made by untwisting the fibres in a yarn, when it will be seen whether they are staple fibres or continuous filaments. In the case of cuprammonium and viscose rayons, although these are usually in the form of continuous filaments, they are also met with cut up into short lengths and spun in the form of staple fibre. The results of the test for different fibres are set out in the table on p. 666.

Twist Test.—This test must be carried out on the individual fibres of the yarn and not on the yarn itself. It depends on the direction of the spirals in the fibre, which are arranged like a spiral spring; in some fibres they are left-handed, and in others right-handed. When a fibre is wetted, the fibre spirals uncoil slightly and coil up again on drying and the direction of the twisting that takes place depends on the direction of the spiral in the fibre. The test is carried out by taking the fibre, wetting it, and holding the free end towards the observer; the direction of rotation of this end, as the fibre dries, is found to be either clock-wise or anti-clockwise, according to the kind of fibre.[1]

Elongation Test.—If the behaviour of fibres on breaking is observed, it will be found that some stretch or elongate to a considerable extent (20 to 30 per cent.) before breaking, whilst others break with scarcely any elongation at all. The results of the test for the different fibres are set out in the table.

[1] Nodder, *J. Text Inst.*, 1927, 13, T 161.

Table of Physical and Chemical Tests

		Burn test.	Staple test.	Twist test.	Elongation test.	Herzberg solution.	Special tests.
Vegetable	Cotton	No ash. No smell	Staple	...	Short	Claret-brown	7
	Linen		,,	Clock	,,	,,	...
	Hemp		,,	Anticlock	,,	,,	...
	Jute		,,	,,	,,	Yellow	4
	Ramie		,,	Clock	,,	Claret	...
Rayon	Cuprammonium		Continuous	...	Long	Purple-blue	5, 6
	Nitro		,,	...	,,	,,	3, 5, 6
	Viscose		,,	...	,,	,,	5, 6
	Sulphur-viscose		,,	...	,,	,,	2, 5, 6
	Lilienfeld-viscose		,,	...	Short		5, 6
	Acetate	Black residue	,,	...	Long	,,	1, 5, 10
Protein	Wool	Black residue characteristic smell	Staple	...	,,	Yellow	2
	Casein		,,	...	,,	,,	...
	Silk		Continuous	...	,,	,,	...
	Tussah silk		,,	...	,,	,,	...
Modified	Mercerized cotton	No ash. No smell	Staple	...	Short	Dark purple	7
	Oxycellulose		...	...	,,	...	9
	Tootal's anti-crease treated		...	...	,,	Very pale purple	8

Herzberg Solution.—The fibres are treated with the solution and the colour is noted. The solution is made as follows :—

(*a*) 20 g. zinc chloride is dissolved in 10 ml. water.

(*b*) 2 g. potassium iodide, 0·1 g. iodine } are dissolved in 5 ml. water.

Mix the two solutions, leave to settle, and decant. Store away from the light.

Fibres should be mounted in this solution and examined with the microscope, using daylight as the source of illumination. The colorations given by different fibres are set out in the table.

Special Tests

(1) *Glacial Acetic Acid* is found to dissolve acetate rayon in the cold, but no other fibre. In partly saponified acetate fibres the unattacked core only will be dissolved, leaving hollow tubular fibres of saponified cellulose acetate.

(2) *Sodium Plumbite.* This reagent can be used to demonstrate the presence of sulphur in fibres by placing them in the reagent and

warming gently. If sulphur is present the fibres turn brown or black. The solution is made as follows :—

To a 10 per cent. solution of lead acetate add 20 per cent. caustic soda solution till the precipitate which forms just dissolves on heating. Fibres containing sulphur are coloured dark brown or black.

(3) *Diphenylamine.* This substance is capable of giving an intense blue colour with nitro-groups, and its use in the present instance depends on its ability to detect in nitro-rayon traces of nitro-groups that have not been entirely removed during denitration. The reagent is prepared by dissolving diphenylamine in concentrated sulphuric acid to a 1 per cent. solution. It is used cold.

(4) *Phloroglucinol.* On moistening first with a 10 per cent. solution of phloroglucinol in alcohol and then with concentrated hydrochloric acid, lignified fibres become a deep crimson colour.

(5) *Differential Dyeing Test.* This test utilizes the different dyeing properties of viscose and cuprammonium rayons ; the two fibres are dyed simultaneously in a dye bath containing suitable red and blue dyes, the blue is preferentially absorbed by the cuprammonium, and the red by the viscose. The dye mixture is made as follows :—

0·2 per cent. solution of Chlorasol Fast Blue FFKS (I.C.I.).
0·2 per cent. solution of Eosin Y.S. (I.C.I.).

The rayons under examination are worked in this bath for ten minutes at room temperature. They are then thoroughly washed and dried.[1]

(6) *Swelling Test.* If a length of rayon with a 5 mg. weight attached is immersed in 20 per cent. caustic soda, changes of length will occur. Again, when the caustic soda is replaced by water, further length changes will take place. These extensions and contractions are different with different types of rayon, and can thus be used as a means of identification.[2]

Rayon.	Length changes.	
	Dry→20 per cent. NaOH.	20 per cent. NaOH→water.
Normal viscose	Extends	Extends
Lilienfeld viscose	Contracts	Contracts
Nitro	Dissolves	...
Cuprammonium	Contracts	Extends
Acetate	No change	Dissolves

(7) *Mercerization Test.* To distinguish between mercerized and unmercerized cotton. The sample must be stripped of all traces of

[1] B.I.S.F.A. Rules for Viscose, Cuprammonium and Acetate Rayon, 1938.
[2] Weltzien, *Textilber.*, 1926, 7, 338.

starch or dextrine fillings and if dyed must be decolorized before the test can be applied. Dextrine can usually be removed by boiling in water alone. But if after boiling in water the sample still shows a blue or purple colour with a very dilute solution of iodine, further stripping becomes necessary; boil for five minutes with a 0·1 per cent. solution of hydrochloric acid or of caustic soda. Some types of starch are very resistant to extraction, and the material may have to be boiled for a few minutes with a 20 per cent. solution of sodium thiosulphate before extracting with acid. If the sample is dyed, an attempt must be made to reduce the colour sufficiently to avoid the iodine coloration being hidden. In order to remove the dyestuff, the material is immersed in a 10 per cent. solution of sodium hydrosulphite and slowly brought to the boil. Further details of stripping methods for different classes of dyestuffs will be found on p. 710.

To prepare the test reagent dissolve 100 g. of potassium iodide in sufficient water to make 100 ml., and in this dissolve 8 g. of iodine. The addition of a larger weight of iodine than this is not to be recommended (Huebner's original paper calls for 40 g. iodine per 100 ml. of iodide solution). The test is no more reliable and takes much longer to carry through to completion than with the weaker reagent. The purified sample is immersed in the iodine solution, together with small cuttings of cotton, one of which is known to be satisfactorily mercerized, and the other not mercerized. After stirring for one minute, the reagent is poured off (and kept for future use), whilst the sample, together with the two standards, is washed in successive changes of cold water, until the washings are colourless. The pieces of cotton, which were a dark brown on leaving the reagent, turn first black and then navy blue as the washing out of the iodine proceeds. Then the non-mercerized sample begins to lose colour, until after about five minutes it is completely decolorized, while the mercerized pattern will retain its blue shade for about half an hour. It will be found that a thick piece of cotton, even though not mercerized, will retain its colour much longer than a thin sample of a mercerized material, but the tone that it retains is brownish, as compared with the true blue of the mercerized standard.[1]

(8) *Tootal's Anti-crease Finish.* Cellulose yarns that have received Tootal's anti-crease treatment can be detected by their behaviour to solvents and swelling agents. Thus they are insoluble in cuprammonium solution which will dissolve all the vegetable and animal fibres. Further, they dissolve only very slowly in 65 per cent. sulphuric acid, which normally swells and dissolves cellulose fibres rapidly. The test with sulphuric acid is best made on a slide under the microscope.

(9) *Oxycellulose Test.* This test depends on the ability of oxy-

[1] Ermen, *J. Soc. Dyers and Col.*, 1931, 47, 161.

cellulose to reduce mercuric potassium iodide solution to metallic mercury, which shows up as a dark stain on the yarn or fabric. The reagent is most useful on rayons since the Harrison reagent described on p. 716 does not differentiate well between materials of different reducing powers where the reducing power is high. The solution is made up by dissolving 100 g. mercuric iodide and 80 g. potassium iodide in 500 ml. water, and to this is added 5000 ml. $3N$ caustic soda. Allow to stand overnight and filter through glass wool.

After removing starch or other foreign matter, test samples are boiled for one minute in the solution, then rinsed in warm 1 per cent. potassium iodide solution, and finally washed in water. Over-bleached or tendered materials show up darker than normal.[1]

(10) *The Ester Test.* This is a more reliable test than burning to detect partly saponified cellulose acetate rayon, or esterified cotton produced by partly acetylating cotton fibres. It is carried out as follows: 0·5 to 1 g. of the rayon is placed in a tube with 5 ml. of 40 per cent. alcoholic caustic potash solution, the tube is heated for a few minutes and 5 ml. of 70 per cent. alcohol added. The liquor is then decanted into another tube, and a mixture of 70 per cent., alcohol 2 parts and concentrated sulphuric acid 1 part, added until there is a slight excess of acid. The mixture is now heated gently, and if there is any acetate present in the rayon, the characteristic fruity smell of ethyl acetate will be observed.

Sizing Materials can be readily detected by means of iodine when they have starch as their main constituent, but some of those now in use on rayon yarns are more difficult of detection. In the latter case the following special reagents will be found useful.

Osmic Acid. Fibres containing size of the linseed-oil type (*e.g.* Boyeux size) can be tested very simply for the presence of this type of size by immersing the sample in a 1 per cent. osmic acid solution for one to three hours. The size will stain an intense brown-black colour. Other unsaturated oils and fats will also stain in a similar manner.

Acid Green. The presence of gelatine size can be easily detected by immersing the sample in the solution whose composition is given below for five to ten minutes, then taking it out and thoroughly washing it in running water.

Mercuric chloride	5 g.
Acetic acid (glacial)	5 g.
Acid green conc. (Meister, Lucius, and Bruning)	2 g.
Water	88 ml.

This stain works best when freshly made, but can be used even after some time. Any gelatine present will be stained an intense green colour, while all the cellulose rayons are left quite colourless.

[1] Rhodes, *J. Text. Inst.*, 1929, **20**, T 55.

Stains on Fabrics can be due to a great variety of causes: chemical or mechanical damage, mildew, oil and lime soap stains, and so forth. Naturally, with such a large variety of causes, no general methods can be laid down, but certain selected methods of detection which have proved useful in practice are given below.

Ultra-Violet Light can be used advantageously for testing for the presence of mineral oil and for certain mildews. Light of a suitable kind for this purpose is produced by passing the light from a mercury vapour lamp through a special filter, which removes all the visible light, and this filtered light gives a striking blue fluorescence with mineral oils, and a yellow or green fluorescence with certain mildews. Sometimes because of the deep colour and great absorption of dyed materials no fluorescence is seen, although a fluorescent substance may be present. For example, this occurs with fluorescent mineral oils, and here a device can be adopted to overcome the difficulty. The fluorescent oil can be transferred to filter paper either by pressure with a hot iron or by damping the filter paper with petroleum ether (pp. 798 *et seq.*). *S.R.A. Red III* can be used to show up oil stains on fabrics other than acetate rayon. The sample under test is put into a solution of the S.R.A. Red containing 1 per cent. of the paste. The sample is worked in this for half an hour at 60°, then taken out, rinsed in water, and dried. The oil stains will be coloured red (p. 713).

Mechanical Surface Damage of fabrics, produced by friction against the sides of kiers and under other circumstances, can give rise to the appearance of "stains." If the damage occurs after the fabric has been dyed, the damaged place appears lighter than the rest of the fabric, whilst if the damage occurs before dyeing, the damaged part dyes and appears darker. The most reliable method of testing in this case is microscopical; however, some indication can be obtained by noting the fluffy appearance of the damaged part, and by the fact that no amount of stripping and extraction with oil solvents will affect the behaviour of the fabric on re-dyeing; the fabric always re-dyes darker in the damaged part when re-dyed with direct dyes.

Neocarmine W. This reagent has been introduced by the firm of Sagar and Gossler as a universal reagent to identify every kind of fibre. It depends on staining different kinds of fibres different colours. It is useful, but cannot altogether be relied on since anomalous results are sometimes obtained.

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III. QUANTITATIVE DETERMINATION OF TEXTILE FIBRES

Textile fabrics met with in commerce may be composed of one or more pure fibres, or more frequently they will contain in addition, starches, dextrines, softeners and mineral matters which have been added with a view to the production of a particular " finish "—stiffness, handle, weight or lustre, to which the pure material could not be made to lend itself. Consequently, before quantitative determinations of the proportions of fibrous materials present in a given sample can be undertaken, it is necessary to make a qualitative analysis of the added finishing matters, followed by an investigation as to the nature of the fibres present. Only when all the various constituents of the sample have been ascertained is it practicable to lay out a scheme for the carrying out of the complete quantitative analysis. (For the examination of textile finishes see p. 858 *et seq.*)

In addition to the actual added foreign matters, the percentage of moisture present must be determined. About 5 g. of the sample is weighed in a weighing bottle, and the bottle and sample then heated in an oven at 110° for about two hours. The stopper is replaced and the bottle and contents allowed to cool in a desiccator. When cold, it is weighed and returned to the oven for another half-hour. If a drop in weight has occurred, the bottle with its contents are heated for another half-hour, cooled and weighed again. These operations must be repeated until a constant weight is attained. The dried sample is next extracted with ether to remove all fatty matters, and then allowed to soak in water at 70° for half an hour, during which time it is well wrung out several times by hand and given a rinse in cold water, before being returned to the hot water. To remove starchy and gummy matters, should such be present, the sample is immersed for one hour at 65° in a 1 per cent. solution of malt extract or other ferment, such as Polyzime, Rapidase or Novo Fermasol, and rinsed in warm water. Finally the material is soaked for one hour in a 0·5 per cent. solution of sodium carbonate at 70°, washed and treated in a platinum basin with a 1 per cent. solution of hydrofluoric acid for one hour at 70°, after which it is washed free from acid and dried to constant weight at 105°. This gives the percentage of pure dry fibre. In order to ascertain what proportion of the total moisture found in the original sample was attached to the fibre and what to the impurities, the purified sample is exposed to the air and weighed at intervals until the absorption of moisture is complete. The difference between total moisture and natural moisture gives the percentage of moisture that had been held by the added finishing materials. The total added foreign matter is the difference between the dry weights before and after stripping.

A portion of the purified material is now weighed out and used for the qualitative examination of fibres present. Should there be more than one kind of fibre to be dealt with, an appropriate scheme of analysis must be devised, so that no damage is inflicted on the residual fibres by the extraction of one of the ingredients of the mixture. The material, purified as described above, is dried and weighed before and after extraction, and the natural moisture determined.

One of the following methods of separation is then carried out, as called for by the nature of the fibres present.

(1) *Cotton and Acetate Rayon.* Extract the dried and weighed sample in a Soxhlet apparatus for one hour with acetone. Dry and weigh. The loss is acetate rayon. The weight of acetate found by difference can be checked by distilling off the acetone extract from a weighed flask and determining the weight of the residue.

(2) *Cotton and regenerated Cellulose Rayons.* 1 gram of the purified sample is extracted at 70° with 100 ml. of a solution of calcium thiocyanate containing 1000 g. per litre of the salt. The mixture is stirred in a flask for one hour by means of a rapidly revolving propeller, filtered through fine copper gauze, washed for half an hour in constant changes of water, and the residual cotton weighed after drying at 110°. Bleached cotton loses 3 per cent. of its weight during this operation, and this loss must be taken into account in the final calculation. Another method depending on the solubility of regenerated cellulose in sodium zincate solution has been devised recently.[1]

(3) *Cotton and Wool.* The sample is boiled for half an hour in a 10 per cent. solution of caustic soda, filtered off through a fine copper gauze, washed with boiling water, then with hot dilute acetic acid and finally with hot water, dried and weighed. The residue is cellulose. An allowance of 3·5 per cent. has to be made on the weight of cotton found, on account of the loss of cellulose on boiling with alkalies. Any oxycellulose present in the cotton owing to previous mishandling will also be dissolved. As a check on the above determination, the sample may be soaked for two hours, at the ordinary temperature, in sulphuric acid of sp. gr. 1·2, when the cotton will dissolve, but the wool is not affected. It is washed well after filtering off the acid and then boiled for fifteen minutes in water. This treatment with boiling water is repeated as long as any acid is extracted. The wool is then steeped in dilute ammonia and washed again with water till neutral. Water alone is not capable of removing all the acid from woollen material. Finally, dry at 105°, weigh, and determine the natural moisture.

[1] Howlett and Urquhart, *J. Text. Inst.*, 1938, **29**, T 43.

(4) *Cotton and Silk.* (*a*) The silk may be extracted similarly to wool, by boiling in a 10 per cent. solution of caustic soda.

(*b*) The silk is extracted by steeping for half an hour in cold, concentrated hydrochloric acid. The cotton is filtered off, washed free from acid, and dried.

(*c*) The silk may be extracted by treating it with a cold ammoniacal solution of nickel hydroxide. This reagent is prepared by dissolving 25 g. of crystalline nickel sulphate in 100 ml. of water, and adding caustic soda solution until nearly all the nickel has been precipitated as the hydroxide. The precipitate is filtered off by suction, washed until free from sulphates, and then dissolved in a mixture of 125 ml. of water and an equal volume of ·880 ammonia.

The sample is immersed in the reagent for one hour and occasionally stirred. The residue of cotton is then filtered off, washed, first with 1 per cent. hot hydrochloric acid, then with hot water till free from acid, dried and weighed.

(5) *Real Silk and Tussah.* The real silk is extracted from the sample with cold concentrated hydrochloric acid for half an hour. Tussah silk is not affected if the extraction is not carried out for too long a time. The residue must be washed with boiling water and ammonia as recommended for wool after extraction of cotton with sulphuric acid.

(6) *Wool and Silk.* The silk is extracted from the sample by a treatment with strong cold hydrochloric acid, or ammoniacal nickel hydroxide (see 4 *b* and 4 *c*).

(7) The estimation of all or any of the above fibres in a mixture fabric is carried out on the lines indicated above, using purified and dry material as the starting point for the extractions.

Fibre to be extracted.	Reagent.
Cellulose acetate	Acetone
Regenerated cellulose silks: rayons	Calcium thiocyanate
Real silk	Hydrochloric acid
Tussah	Ammoniacal nickel hydroxide
Wool and hair	Caustic soda 10 per cent.
Cotton	Not extracted

IV. MECHANICAL TESTING OF TEXTILE MATERIALS

By H. A. Turner, M.Sc., A.I.C.

A. Measurement of Fineness, Count, or Denier in Yarns

All the methods suggested for this measurement require the determination of the length and the weight of a given piece of yarn. The methods vary in detail as the quantity of the sample is large or small. On account of the inconvenient units used in the traditional methods of expressing calibre, making it difficult for mill-operatives,

etc., to work out the results of a straightforward determination by weighing and measuring, modifications have been introduced to enable the count to be read off directly. These require specially constructed weighing and measuring apparatus. For general purposes, however, the weighing apparatus may be an ordinary chemical balance, where quantities of yarn not less than 0·1 g. are available. One of the many conveniently operated patterns of torsion balance (weighing to a maximum of 50 or 25 mg., and manufactured by most well-known chemical balance manufacturers) may be used when only short lengths of yarn are available.

For accurate determinations of the count or denier three things are necessary: accuracy in the determination of length, accuracy in weighing, and control of the moisture content of the sample of material.

Where large samples in great number require measurement, the operation is best carried out in a chamber of controlled humidity, smaller samples being kept in desiccators containing chemical mixtures to maintain a constant fixed humidity,[1] measured off, and weighed for counts. At the same time another portion of the sample may be weighed out, placed in a large weighing bottle, and heated (with the stopper of the bottle partially displaced) in an air oven controlled at 105°. At intervals the stopper of the weighing bottle is replaced and the bottle removed and allowed to cool in a desiccator over concentrated sulphuric acid, and then weighed as rapidly as possible. When the weight of the bottle reaches a constant value it is assumed that the whole of the moisture content has been removed. In this way the moisture content of the original sample is determined and the weights of the measured portions taken for count may be converted either to the weight of bone-dry material (giving the absolute count) or to the weight the material would possess if it contained a standard percentage of moisture. This quantity of moisture, which forms the basis on which transactions are carried out, is called the *Regain*, and it is the mean increase in weight of 100 parts of perfectly dry material which ensues when it is allowed to come into equilibrium with the atmospheric moisture in an atmosphere whose relative humidity is 65 per cent.

The accepted *Regains* for a number of typical materials are—

100 g. of bone-dry grey cotton becomes 108·5 g. at 65 per cent. R.H.
100 ,, ,, mercerized cotton becomes 110·0 g. at 65 per cent. R.H.
100 ,, ,, viscose rayon ,, 112·0 ,, ,, ,,
100 ,, ,, silk ,, 111·0 ,, ,, ,,
100 ,, ,, flax ,, 112·0 ,, ,, ,,
100 ,, ,, worsted ,, 118·25 ,, ,, ,,
100 ,, ,, wool ,, 116·0 ,, ,, ,,
100 ,, ,, acetate rayon ,, 106 ,, ,, ,,

[1] *E.g.* ammonium nitrate will furnish a R.H. of 65 per cent. at 17°. For mixtures giving other R.H., see H. M. Spenser, *International Critical Tables*, New York, 1926, vol. i., p. 67.

Yarns made from natural vegetable fibres or from wool, that is, spun yarns, have their fineness expressed as the length of a given weight, or the *count*. Silk and rayon continuous yarns have their fineness expressed as the weight of a given length or the *denier*. The actual values taken for unit weight and unit length vary with the different materials. Often, with the same textile material, they vary according to locality, the Macclesfield, Manchester, Lyons, and International Silk denier being all different. There is, however, a tendency to accept one count or one denier as generally applicable to one particular kind of textile material.

The following are the principal counts in general use :—

English Count for Cotton Yarn, Spun Silk, and Rayon Staple Fibre

The count of a single yarn is given by the number of 840 yard hanks which will weigh together exactly 1 lb. *E.g.* in 20/1 or "twenties," 20 such hanks weigh 1 lb. The count of a folded yarn is expressed in terms of the counts of its single components, *e.g.* 20/3 contains three 20/1 yarns twisted together. Disregarding the contraction due to twisting, 20/3, *i.e.* 6·67 hanks of this yarn would weigh 1 lb.

Where short lengths of yarn are measured in cm. and weighed in grammes the count is given by

$$\text{Count} = 590 \times \frac{\text{L. cm.}}{\text{Wt. g.}}$$

Other counts are calculated as for the English, except that units of length and weight are different.

	Length.	Weight.
International	1000 m.	1000 g.
French	1000 m.	500 g.
Austrian	1159 m. or 1267·6 yds.	560 g. (1 Pfund)
Dutch	840 yds. (Eng.)	500 g.

The cotton count is also used for spun floss silk and for rayon staple fibre.

Irish Count for Linen, Tow, Jute, Hemp and Ramie

This count is most widely used. The singles count is the number of 300 yard hanks in 1 lb.

Scottish or Belfast Count for Jute

Is really a denier and is the weight in pounds of 14,400 yards or 13,167 metres.

Wool Counts

Worsted Count. Number of hanks 560 yarns in length in 1 lb. Folded yarns are reckoned on the counts of the singles as in cotton and are expressed, 2/30, etc.

Woollen Count (Yorkshire). Number of hanks (256 yards) in 1 lb.

Other wool counts are—

	Length unit.	Weight unit.
Berlin	1467 m.	467 g.
Saxony	1467 m.	500 g.
Austrian	1371 m.	560 g.
French, Sedan	1493·6 m.	500 g.
French, Elbœuf	3600 m.	500 g.

The international count, units 1 km. and kg., is applicable to all the materials given above.

Denier. The legal or international denier is very widely used for thrown silk, degummed and dyed yarn, and continuous filament rayon. It is the weight in grammes of 9000 metres of yarn.

Different and less commonly used deniers are the Turin, Lyons, French, Macclesfield and Manchester.

Determination of Count or Denier

If the yarn is in hank form, it is shaken out carefully and placed on a smoothly running hank carrier (swift or ryce). The automatic expanding type made of light wood or smooth metal is to be preferred to any other variety. The tie-bands are removed carefully to avoid unsettling the lie of the strands, the ends are broken and the end which leads to the top layers of the hank is pulled off for several yards until the yarn is unwinding smoothly. The yarn may then be attached to the special wrap reel. The wrap reel has a circumference which normally bears some simple relationship to the length unit used for the count determination. For example, for cotton yarn the circumference is 56 ins. and the quantity taken for a count determination is 80 turns on this reel (120 yards), which is 1 lea or one-seventh of a hank. For coarser yarns or with restricted samples half or quarter lea quantities are wound off.

The reel itself is most often wound by hand and consists of six spokes of equal length fixed radially round an axle. At the end of each spoke, a smooth metal bar is arranged with its edge parallel to the central axle. The yarn thus forms a hank of hexagonal elevation when wound on to the bars of the reel. Coupled by a worm gear to the reel is a bar which carries glass " pigtails " or yarn guides, and, by slowly traversing the yarn as it is wound, lays the individual turns of the yarn parallel to and almost touching each other on the

bars of the reel. A revolution counter is attached to the reel, and is so arranged that a gong sounds at the end of each 80 revolutions.

It is essential that the reel should start up without jerk and should be operated at a uniform speed during the winding. To avoid irregular tensions in the yarn as well as fatigue in the operator, it should be perfectly symmetrical and should be balanced carefully on its axle. The bars should be machined carefully to ensure that neither sharp edges nor rough places remain. Since these reels are more readily maintained in uniform rotation when they are fairly heavy, they are preferably of rather massive construction. This also guards against warping and deformation. It is necessary to see that the base is made sufficiently heavy so that the act of rotation does not cause the whole apparatus to slide about on the bench. Any gears incorporated in the winding mechanism or in the traversing motion should not be in a dangerously exposed position, nor should they be so placed as readily to pick up lashing ends of yarn. To prevent erratic unwinding of the swift, it is frequently braked by slipping a loop of leather strap, rough side inwards, over the wooden spindle. The strap carries a small lead weight. This weight should be sufficient only to exercise a gentle checking action upon the swift. It will naturally require to be greater the coarser the yarn.

When the yarn is in a chase-wound package, *e.g.* cop, pirn, bottle bobbin or canette, it is conveniently unwound by placing the package vertically with the nose upwards at a level rather below that of the reel. The thread is led from this package vertically upwards to a horizontal glass rod and over this at right angles so that it goes to the reel approximately in a horizontal direction. Bobbins and cheeses are threaded on a smooth horizontal rod disposed at such a height that the yarn goes horizontally to the reel. For bobbins with small smooth-edged flanges it is often possible to unwind over the end like a cop. Since the yarn winds from these packages in an irregular fashion, it is often advisable first to pass the yarn through a "scissors" type drag (such as is used on many pirn-winding machines). This will help to render the tension more uniform. As has been stated in the section on strength testing, the lea hanks may be used for a lea-strength test before weighing for counts.

Where short lengths of yarn are to be measured, it is necessary that they should first be placed under a slight but definite tension in order to straighten out any crimp, snarls, loops, etc. A simple and convenient procedure is to fasten a metre rule vertically upon a wall. Near the upper end a small hook should be screwed. One end of the yarn is fastened into a small bull-dog clip which is suspended on the hook. To the lower end of the yarn is fastened another bull-dog clip of appropriate weight. The yarn thus hangs under tension against

the scale. The required length is marked off on the yarn, and the yarn is then removed from the clips and cut with a razor-blade or sharp scissors at the markings. This yarn may now be weighed on a torsion balance. Here a few simple precautions are necessary. The yarn to be weighed should hang freely from the hook, and the whole balance should be protected from draughts during the weighing operation. As the weight of the sample will be very small, large errors can be introduced by handling directly with moist fingers. The yarn should always be handled with forceps. Calculation may be simplified by taking a length bearing some simple relation to the unit length in the count-system employed, *e.g.* for denier, 90 cm., for cotton counts, 59 cm., etc.

Crimp Measurement. The arrangement for measuring under tension just described is also convenient for measuring the crimp of warp or weft yarn in a woven piece. The crimp is usually expressed in the following form—

$$\frac{\text{length extended} - \text{length in woven cloth}}{\text{length in woven cloth}} \times 100.$$

The determination is carried out by drawing on the cloth two ink lines a convenient distance apart (say 20 cm.) at right angles to the yarn to be examined (*i.e.* weftwise if the warp is being measured). The marked threads are then removed carefully from the cloth, suspended between the bull-dog clips, and the distance apart of the two marks measured on the scale. A similar determination may also be carried out with knitted fabric, the marks being then made at right angles to the rounds of knitting. The uniformity or non-uniformity of crimp of successive threads or rounds often supplies valuable information of the degree of regularity of warping, winding, weaving or knitting tensions in the yarn composing the fabric.

Yarn Regularity. The measurement of regularity in count, diameter or twist as a routine operation is perhaps more strongly the business of the producer than of the general investigator. There are, however, occasions when irregularity in one or the other of these properties is responsible for a faulty appearance in fabrics, and this may on the surface be indistinguishable from that caused by defective dyeing. Such faults may often be investigated by simple means. Point-to-point variations in count may be measured by cutting out small standard lengths of the yarn (observing the precautions described in the section on count determination) and weighing on a delicate torsion balance. Diameter may be measured by leading the yarn, under a suitable small tension, through guides fixed on the stage of a microscope fitted with a micrometer eye-piece. A similar arrangement serves to measure point-to-point variations in twist factor. In this apparatus

the micrometer eye-piece is replaced by one fitted with a hair-line across a diameter of the field. The eye-piece is rotated until the hair-line coincides with the line of the twisted fibres. Attached to the eye-piece is a pointer which travels over a sector scale graduated in degrees, and the rotation of the eye-piece can thus be measured. In this way the angle made by the fibres with the axis of the yarn is determined and the local twist is proportional to the tangent of this angle.

A number of different instruments have been suggested for the continuous measurement and recording of the variations in diameter of long lengths of yarn. In one designed by the Woollen and Worsted Industries Research Association [1] the yarn passes in front of an illuminated slit. According to the diameter of the yarn a greater or less proportion of the total area of the slit is covered. The light which escapes through the uncovered portion is allowed to fall on a photocell, and the fluctuations of the current in this cell are recorded mechanically on paper which is moved along by a mechanism which is coupled with the mechanism which moves on the yarn.

In the instruments designed by Viviani [2] the yarn is led through a capillary in which the bore exceeds the yarn diameter. In one form, the remaining space in the tube is filled with mercury. The fluctuations in the volume of this thread of mercury caused by the fluctuating diameter of yarn is measured by determining the electrical conductivity. In the other pattern, air from a reservoir is allowed to escape through the capillary. Its flow is controlled by the diameter of the yarn partially blocking the capillary and fluctuations in the flow are suitably recorded. In other apparatus, the yarn is drawn through a V-shaped slit under very slight tension. The finer the yarn the lower the position it will take up in the slot. The movement of the yarn up and down the slot is recorded photographically. Earlier apparatus proposed to measure the diameter by pulling it between the contact plates of a dial micrometer, but, owing to the pressure exerted on the yarn by those plates, the measurements were more a record of the fluctuations in softness of the yarn.

It is, of course, impossible to obtain a truly continuous record of yarn strength. The Moscrop machine (*q.v.*) gives a record of the strengths of successive short lengths of yarn in the correct order. H. Dietz [3] has devised a machine which will record the number of places at which the strength of a length of yarn falls below a predetermined value.

[1] Stanbury, *J. Text. Inst.*, 1928, **19**, T 405 ; 1931, **22**, T 385.
[2] *Kunstseide*, 1931, **13**, 281, 321.
[3] *Monatsschr. Textilind.*, 1929, 335.

Cloth Counts

The counts of a cloth are the respective number of warp threads (or ends) and weft threads (or picks) per unit length (1 in. or 1 cm.).

Often they are simply counted by laying a ruler across the particular set of threads to be examined. For finer cloths the use of a magnifying glass is to be recommended. The type called a count glass is convenient. A metal plate is laid on the surface of the cloth. In the plate is cut a square, rectangular or cruciform hole whose respective sides measure 1 in., ½ in., or such convenient length. Fixed above the plate, so that the cloth seen through the hole is in focus, is a magnifying glass. Many elaborate variations of this glass are made, but the simpler form, which can be kept in the pocket, is adequate for most purposes. The count is made by determining the number of threads crossing at right angles one of the sides of the hole. The mean of several such determinations is taken to define the cloth.

It may be necessary, in investigating irregularities of appearance, to determine the individual distances apart of successive warp or weft threads as they lie in the cloth. This is most conveniently carried out on the microscope using a low-power (1 in.) objective and a micrometer eye-piece with a boldly marked scale (the echelon type of marking is very suitable). A strip of the cloth is stuck squarely and without distortion to a glass microscope slide, and when the whole of the threads which cover the micrometer scale have been examined the slide is moved by a mechanical stage into a fresh position. If a travelling microscope is available, and the graduations of the scale are sufficiently fine, the end or pick distances may very conveniently be measured by it on long lengths of cloth.

In using a microscope for cloth counts the material is most conveniently examined by reflected light. A couple of reading lamps of the type in which the bulb is carried on a long flexible stem are useful accessories. In most cases a strongly oblique lighting which defines the constituent threads by sharp contrasts of light and shade is to be preferred as less fatiguing to work by. The lamps may be adjusted over the surface of the cloth according to its structure. Many of the more elaborate forms of adjustable illuminator especially designed for microscopy may also be used.

If a large piece of cloth is to be examined by a travelling microscope it should be laid flat on a table, all creases should be smoothed out, the warp and weft arranged accurately perpendicular, and the portion to be examined should be fastened to the table with pins placed at close intervals so that the threads may not be distorted. As an alternative, the cloth may be held down by pieces of metal bar of a convenient size, on the underside of which a strip of baize or other

rough cloth has been pasted. Smaller pieces of cloth may often conveniently be held in a large photographic printing frame. Successive measurements of the distance apart of the picks of weft over fairly long lengths of the cloth are resorted to, for example, in the investigation of periodic irregularities in the weave of the cloth which may have given rise to a stripy appearance in the dyed material. The pattern observed is frequently caused by bands of closely packed weft alternating with bands in which the weft threads are less close together. The results are conveniently recorded directly on graph paper, the distance apart of the pick being plotted along one ordinate and the serial number of the pick along the other. If the peaks of the resulting curve correspond in arrangement to the pattern of stripes on the material, the connection between the appearance and the structure is established. These periodicities are often complicated, being the resultant of a number of superposed simple periodicities. The pattern may often be analyzed into its components by plotting first the distance apart of single picks, then of successive groups of, say, 4 picks. The operation is repeated with 8 pick groups, 12 pick groups, etc. In this way the effects of the periodicities of shorter frequency are successively eliminated, and finally the frequency of the longest simple periodicity is obtained.

A very interesting instrument, the Lunometer, has been developed by its producers (Firma P. Luka, G.m.b.H., Barmen) for use in many determinations where the local count of cloth and the diameter of yarn is to be measured.[1] It consists of a rectangular sheet of plate glass at right angles to whose length is drawn a system of parallel lines, the distance apart of these lines gradually decreasing from one end of the plate to the other (*e.g.* twenty-five lines to the inch at one end and sixty at the other). A scale by the side shows the closeness of the lines at any particular part. When this plate is laid on a piece of cloth with the lines parallel to the warp or the weft threads, a series of bands appear due to interference between the parallel threads and the lines on the lunometer. These bands are very narrow where the spacing between these threads and that of the lines are very dissimilar and gradually widen to the position on the grating where line spacing and thread spacing are approximately equal. At this point, therefore, reference to the adjacent scale gives the spacing of the threads. More complicated patterns are set up where the spacing of the threads in the cloth is irregular, and from these patterns further information about faults in picking or in warping may be obtained. By winding yarn under uniform tension on to a rectangular card in such a manner that each turn of yarn

[1] *Mell. Textilber.*, 1929, 705 ; 1930, 273. The apparatus is listed by Messrs Gallenkamp, London.

touches the adjacent one, and then by inspection of the wound pad under the lunometer, the diameter of the thread may be estimated, while irregularities in diameter are shown up. For full information of the application of this instrument, reference to the original paper should be made.

Identification of Warp and Weft. When the selvedge is included, it is simple to determine which are warp and which weft yarns in a given sample, the warp being parallel to the selvedge.

In plain cloths, and cloths at once recognizable as poplins, if the warp and weft are dissimilar in diameter or twist, the softest and coarsest yarn is the weft. In grey cloth, the warp may often be shown up by treatment for a few minutes in warm water, followed by very dilute iodine solution. The starch used in sizing gives a blue stain. If, in a finely ribbed cloth, the adjacent threads in one direction appear to take independent courses, while those in the perpendicular direction appear to have been incorporated in the weave in pairs, the cloth is a common repp, and the paired threads form the weft. Sometimes one set of threads in a fine open cloth appear to be strictly parallel, while the perpendicular set converge at places. The latter are likely to be the weft threads.

In a plain cloth with similar yarn in warp and weft, the threads with the most crimp are likely to be the warp threads.

Although there are many exceptions, it is still a convention, particularly with plain cloths of staple pattern, that the warp threads shall be twisted with a right-hand twist (*i.e.* a thread may be untwisted by turning one end in an anti-clockwise direction), whereas the weft has a left-hand twist. In many fabrics, including the majority of crepes, the warp threads have all the same twist while the weft is composed of alternate right and reverse yarns.

B. Measurement of Twist of Yarns

In cotton, staple fibre, bast fibre and worsted yarns there may be two twists to examine, the spinning twist of the singles yarn and the doubling or folding twist with which two or more singles yarns are folded together.

The determination of folding twist is relatively easy to carry out. Often it may be done by making the strand taut under a light tension on a table and counting the turns in 1 in. by means of a count glass, remembering that in a twofold yarn two " humps " correspond to each turn of twist, three in a threefold yarn and so on. Alternatively a twist tester may be used. The twist tester adapted for determining folding twist consists of a long rectangular base. At one end is a fixed pillar carrying a headstock with a spindle to which is attached a pair of rotating jaws. The spindle is moved by a hand-wheel

through a gearing for increasing the speed of revolution, and is connected with a revolution counter. Some distance away is another pillar carrying a pair of fixed jaws. This pillar is capable of being fixed in the base at various distances from the headstock, so that the distance between jaws may be varied and lengths of yarn 2, 3, 6, and 10 in., etc., may be tested. The whole arrangement is like a simple lathe in construction. In many designs, beyond the fixed jaws is a pillar carrying a smooth pulley. The yarn to be tested is clamped in the centre of the movable jaws at some distance from the free end of the yarn (since the twist tends to run out where the yarn has been cut) and, after clamping, the free end of the yarn is cut away. The yarn is then brought through the opened fixed jaws, and over the pulley behind. Immediately behind the pulley a light weight is clipped on to the yarn to provide a standard straightening tension. When the yarn is taut, the fixed jaws are closed. The rotating jaws are then turned by means of the hand-wheel in a direction which will untwist the yarn, and the jaws are rotated until a needle inserted between the single threads at the fixed jaw can be passed freely along the full length of yarn. The number of turns required to untwist the yarn divided by the length of the test piece gives the original folding twist in turns per inch.

The same procedure may be used for continuous filament yarns provided that the original twist has not been too great. Highly twisted silk yarns are often difficult to untwist sufficiently to enable a needle to be passed among the filaments from one end of the test piece to the other.

For singles yarn spun from fibres and for highly twisted continuous filament yarns a different procedure has to be employed. For the latter and for long fibre materials an approximate value may be obtained in the following manner. The twist tester just described is modified so that the non-rotatable jaws are capable of slight movement along the axis of the thread being tested. The movement inwards of this set of jaws is opposed by a light counter weight, and the extent of the movement is registered by means of a pointer passing over a scale. The test piece is inserted in the instrument under a slight tension so that it exerts sufficient pull upon this set of jaws to bring the pointer to zero on the scale. As the yarn is untwisted it expands and the non-rotating jaws, under the action of the counter-weight move outwards, the pointer showing the movement. When the twist is removed completely, the length of the test piece reaches approximately its maximum value. As the rotating jaws are turned, still in the same direction, the yarn acquires twist of the opposite kind to that it possessed originally and begins again to contract. The rotation is continued until the length of the test piece reaches its

original value, and the pointer is brought back to zero. At this stage it is assumed that the yarn has acquired the initial degree of twist but in the reverse direction. If this is true, then the original number of turns of twist in the length of yarn under examination will be half the total number of rotations that have been given to the rotatable jaws. The values obtained by this method may be very approximate. When the yarn is almost untwisted it is a very loose assemblage of fibres or filaments which may themselves be incapable of complete parallelization. They are, however, often capable of independent movement, so that the untwisted yarn expands irreversibly under the tension applied. Owing to imperfect cohesion, the loose assemblage is unable perfectly and uniformly to transmit the twisting effect, imparted at one end, along the whole of the test piece. Knots, tangles of broken filaments, neps, etc., all interfere seriously with the accuracy of this method. In certain cases, however, it is the only one applicable.

For short-fibre single yarns (*e.g.* cotton) the looseness and lack of cohesive properties of the untwisted yarn render yet another modification of the method desirable. The construction of the twist tester is very similar to that first described, but the distance between the two sets of jaws is preferably rather less than the mean staple length of the yarn fibre (*e.g.* 1 in. is a convenient distance for many cotton yarns). Many of the fibres constituting the test piece are gripped at both ends, and practically all of them are gripped at one end or the other. Untwisting is carried out in the normal way, while the centre of the test piece is examined under a magnifying glass. Untwisting is stopped when the fibres appear to be parallel. It is sometimes difficult to judge when this point is reached, particularly if the yarn is initially of high twist, but operators soon become expert. The mean of fifty or more single determinations is necessary for a representative value for the yarn when such short lengths are taken, since in spun yarn the twist is normally a very variable quantity.

Nomenclature. Threads which have a right-hand twist (*i.e.* untwisted by turning in an anti-clockwise direction) are said to be twist or right yarns. Those twisted in the opposite direction are called weft or reverse yarns. A yarn in which both the single and the folding twist is right-handed is often referred to as a twist-on-twist or T.O.T. yarn. Where the singles are right-handed and the doubling twist is left-handed the yarn is referred to as weft-on-twist or W.O.T.

Twist Factor. Except for the purpose of distinguishing yarns, the expression of the twist in terms of turns per inch or turns per centimetre is not an ideal general method since, unless the count is stated, it gives no information about the spiral structure and tightness of the yarn. It will be seen that one turn given to a fixed length

of yarn has a greater torsion effect, and imparts a closer spiral formation to the constituent hairs or filaments when the yarn is coarse than when it is fine. If therefore the true twist in yarns of dissimilar diameter is to be compared on a common basis, the pitch of the twist spiral is the important quantity. This quantity is expressed as the twist factor,

$$a = \frac{T}{\sqrt{c}},$$

which is approximately proportional to the tangent of the angle made by the spiral with the longitudinal axis of the yarn.

In the majority of yarns the twist (T) is expressed in terms of turns per inch and the count (c) as the English count for the material under consideration. This expression is not strictly correct because it assumes a relation between count and diameter of the yarn which does not hold completely for yarns of all twists and, in the case of cotton, for all varieties and staples of the material. Values derived by its use are sufficiently close to the truth for most practical purposes.

C. Tensile Tests

Testing of the tensile properties of textile materials may take place at any of the states of aggregation met with during manufacture, from that of the single fibre to that obtaining in a finished fabric. This includes the intermediate stages of sliver, slubbing, roving, single and folded yarn, yarn in the form of bundles or hanks, and cloth in the form of strips.

Strength.—The most common expression of the magnitude of mechanical resistance to stress is made in terms of the *Breaking Load.* For the determination of this quantity it is usual to clamp a sample of specified dimensions between two jaws or some similar mechanical arrangement. One of these jaws is held stationary while to the other a steadily increasing force is applied in the direction of the line joining the centres of the two jaws. The value of this force at the moment when rupture of the sample takes place, is called the breaking load. It is usually expressed in units of mass, such as the ounce, the pound, the gram or the kilogram. It is rare to find it expressed in dynes or in the more scientifically correct terms of force per unit cross-sectional area. Generally speaking, the determination of the absolute value of the tensile strength is unnecessary, since the sample is, almost without exception, compared in behaviour with a material real or ideal which acts as the standard and which has been, or is assumed to have been, tested under exactly similar conditions. To determine the true cross-sectional area of a sample of material of complicated

structure such as a yarn or a fabric is not easy. Of a number of yarns of different calibre, but composed of the same fibrous material, and possessing the same effective twist (see "Twist factor," p. 685) the respective strengths will increase as the yarns become coarser. As a first, and very rough approximation, it is assumed that the increase in strength is inversely proportional to the count or directly proportional to the denier (*q.v.*). Yarns of different calibre are often compared for intrinsic strength by employing a fictitious quantity known as the "breaking length" which makes use of the assumed proportionality.

The Breaking Length.—The breaking length is that length of yarn which, if suspended freely by one end, would break under its own weight. The calculation of this quantity is made clear by an example. Suppose a cotton yarn of 60's count (*i.e.* a yarn of such calibre that sixty hanks each containing 840 yards are required to make up 1 lb.) requires on an average the application of a force of 1·2 lb. weight for the rupture of each strand. Then the breaking length would be $1{\cdot}2 \times 60 \times 840$, *i.e.* 60,480 yards. Where the method of expressing the calibre is in *denier* the breaking length is calculated by dividing the mean breaking load of one thread by the denier. For example, if yarn of 120's denier has a mean strength of 150 g. per strand, the breaking length will be $\frac{150 \times 9000}{120}$ metres.

Strength per Calibre. Breaking lengths are thus essentially quantities in which the breaking load is divided by a figure representing the coarseness (weight per unit length) of the yarn. Similarly derived quantities for wool and cotton are the so-called "count × strength product"; and for silk and rayon, "breaking load in grams per denier." The use of these quantities assumes that, on an average, the number of constituent fibres or filaments in the cross section of the yarn will be directly proportional to the coarseness, and that when rupture takes place, it will be brought about by the simultaneous fracture of all the constituent filaments or fibres at the point of rupture. In making these calculations, therefore, the yarn strength is assumed to be a simple summation of the individual fibre strengths. The processes of fracture, in yarns made from continuous filaments, *e.g.* silk and rayons, resemble most nearly this ideal process and therefore figures for the specific strength have greatest validity with these materials. The breaking processes of spun threads made from short-length fibres are very complicated, and quantities such as the breaking length must be employed with caution.

Heerman-Herzog gives the following values for the breaking lengths of yarns of different fibrous materials. These figures will be influenced enormously by the origin of the raw material and its initial condition,

the nature of the preparation and spinning processes, and the ultimate structure of the yarn.

Breaking Lengths of Yarns

Material.	Breaking length in km.	Count × Strength.
Wool . . .	8·5	0·0165 Eng. wool count × lb.
Mohair . . .	11·5	0·0225 ,, ,, ,, × ,,
Cotton . . .	25·0	0·0324 ,, cotton ,, × ,,
Ramie . . .	33·0	0·119 ,, linen ,, × ,,
Flax . . .	52·0	0·187 ,, ,, ,, × ,,
Hemp . . .	55·0	0·198 ,, ,, ,, × ,,
Jute . . .	32-34	0·119 ,, ,, ,, × ,,
Silk . . .	30·0	3·33 g. per den.
Rayon . . .	8-10	1·00 g. ,,

(Modern Rayons at least 50 per cent. greater)

With fabrics knitted or woven, the *bursting strength* is sometimes determined. This is the force which, when applied to a definite area of the material in a direction normal to the surface, is just sufficient to cause rupture. The measurement of bursting strength is borrowed from the testing procedure for paper, where the point-to-point resistance of the paper is normally fairly uniform and the extension under stress is low. There are many limitations to its application to cloth, particularly where the warp and weft yarns are very dissimilar in strength or extensibility. The material will then burst by tearing across the weaker or the least extensible set of yarns. Nevertheless the bursting test does serve to indicate the probable reaction of the material towards certain of the destructive influences encountered during use.

Extension and Extensibility

On loading textile materials extension occurs. This is due in part to an extension of those constituent fibres or filaments which have a directional component parallel to the direction of the loading force; in part, to a straightening out of spirally disposed fibres in spun or twisted yarns. In fabrics there is also a straightening out of the zig-zags or loops of the constituent yarns (the so-called *crimp*) as they are normally disposed in the fabric. Thus the extension mechanism of compound structures such as yarns or cloths may be very complicated. As will be shown later, the load-extension relationship for fibres, yarns, and fabrics can often yield valuable information about the previous history of the material. The regularity of this relationship as between one test piece and another has an important influence on the general behaviour of the batch. For instance, if a cloth is woven from yarn of irregular extensibility and is then subjected

to stress, the strands of low extensibility will take up a large proportion of the total stress and this may be sufficient to bring about their rupture. If, however, the cloth has been woven from yarn of the same mean breaking strength but of regular extensibility, the stress on the cloth is evenly distributed among the constituent threads and the stress for any one thread is much less likely to reach an excessively high value.

Many machines record only the extension at break. The machine usually shows the increase in length of the test piece, but it is better to calculate from this and from the original length of the test piece the *percentage extension at break* and to return this figure.

One of the most important factors which determine the strength of a yarn is the effective twist or twist factor (see p. 685). In yarns made up from fibre of relatively short length, *e.g.* cotton, the yarn with low twist is always weak owing to the ease with which the constituent fibres may slip past each other. Increasing twist, in virtue of its effect in clamping together the constituent fibres, brings about increasing strength until a certain limit is reached (with cotton yarns of most kinds this occurs when the singles twist factor is about 5). For yarns of higher twist factor the increasingly tight packing of the constituent fibres leads to them being subjected to longitudinal and shearing stresses as a result of the twisting action alone, and the ultimate result is a weakening of the yarn as a whole. Furthermore, the tight clamping of the constituent hairs in highly twisted yarn decreases its resistance to those of the stresses met with in use which can be relieved by an extension due to the partial slippage of one hair past another. The effects of increasing twist on continuous filament yarns is more complicated, but it results in an increase in strength up to the point where a certain maximum twist factor has been reached, after which, like cotton, the strength diminishes. Unlike the short filament yarns, however, the extensibility continues to increase with increasing twist long after the point of maximum strength has been passed.

Conditions of Testing

Speed of Loading. The value of the breaking load and of the extension depends upon the rate at which the stress is increased. When certain kinds of fibre are being tested (*e.g.* wool) it is known that a modification of the molecular structure takes place. In an analogous manner the fibres in yarns undergo relative positional adjustments, depending on the yarn structure, when stress is applied. The constituent yarns of fabrics also alter their relative positions with consequent changes in the proportions of the total stress they carry, and of the frictional forces between them. If the load is applied very rapidly these adjustments have not time to take place before rupture

occurs, while, at the other extreme, very slow loading allows full adjustment to occur. Most of the machines used for testing the tensile strength of textile materials cause the load to be increased relatively slowly. It is therefore necessary to provide mechanical arrangements to ensure that the load is applied in a uniform manner to each test piece.

As the load upon a fabric yarn or fibre increases, the same increment of load will produce different increments in the extension of the material. With spun yarns, the relation between load and extension is often very complicated, being influenced both by changes in the yarn structure and by the characteristic behaviour of the component fibres. With single fibres or with continuous filament yarns it is often possible to relate the characteristics of the load-extension curve with the intimate structural changes in the fibre-substance or with the previous history of the fibre. This has been done, for instance, with a good deal of success by Speakman and Astbury for the protein fibres. For investigations of this kind, apparatus in which either the rate of loading or the rate of extension is maintained constant may be necessary. In most of the machines, to be described later, in practical use for routine testing, neither rate of loading nor rate of extension is maintained constant since this requires more elaborate construction. A compromise is usually made so that simplicity of operation is combined with a reasonably regular application of the load to each test piece.

It is, in general, easier to construct an apparatus in which the rate of loading is constant than one in which the rate of extension is maintained steady. The latter form of apparatus presents difficulties when testing fibres such as wool and viscose rayon which have phases of elastic extension (accompanied by relatively high resistance to stress) preceded or followed by a long phase of plastic extension. Here, unless the time of making a test is unduly prolonged, the rate of loading during the phases of elastic extension has often to be very high, and this may not allow the satisfactory adjustment of internal structure to applied stress to take place. In investigating technical faults, particularly in rayon materials, defects in production of the fibre, weaving, processing, inappropriate treatment during use, etc., may often be detected by detailed examination of the stress-extension curves, and these are more readily interpreted if the rate of loading has been maintained strictly constant.

Moisture Content. The breaking load of all textile materials is dependent upon the moisture content of the material. This is, in turn, dependent upon the moisture content, expressed as the relative humidity, of the air with which the sample has been in contact prior to the moment of testing. For any one species of fibrous material, an

equilibrium is reached ultimately between the moisture content of the material and the humidity of the air. When the initial moisture content of a material does not correspond to the moisture content which would be in equilibrium with that of the surrounding atmosphere, some time may be required before a new equilibrium is established. In order to obtain consistent and reproducible results, it is advisable to carry out testing operations in a room in which the relative humidity of the atmosphere is maintained at a fixed value, and also to make sure that the samples are kept in this room some hours before the test is carried out. If the construction of a constant humidity room does not appear to be warranted, somewhat less accurate control, which is adequate for many purposes, may be exercised by keeping the samples to be tested in a small enclosed space in which the relative humidity of the atmosphere is kept at a steady value by the presence of equilibrium mixtures of salt hydrates, etc., removing the samples only as they are required for testing. By choosing the testing room so that it has no direct contact with the outer air, and by ensuring that it is not subject to rapid fluctuations in the room temperature the disturbing effects of wide variations of the moisture content of the test samples may to some extent be avoided. If it is desired to compare the tensile behaviour of two or three different materials, by testing in a room in which the relative humidity is not controlled, it is better to store them side by side for some hours, and then to carry out the tests on the whole group with as little intervening delay as possible.

The method of testing yarn or cloth in the wet condition in order to eliminate the effects of variations of moisture content is sometimes employed, and it may be useful for comparative measurements in special circumstances. Complications are introduced if there is present any water-resisting substance upon the material, particularly if, as frequently occurs, this substance is irregularly distributed. The strength of all materials is altered on wetting, and with viscose and cuprammonium rayon an appreciable decrease results. This makes it necessary for the exercise of increased caution in handling the materials during the testing operation, in order that the test pieces may not be stretched or weakened. Since the modifications brought about in the fibre, yarn, and fabric structure by wetting do not take place instantaneously, it is necessary for the test pieces to be left in contact with distilled water, for a period not less than half an hour. It must be remembered that wetting may cause a more or less complete elimination of strains set up during the previous treatment of the material, and more information of its history might be furnished by tests upon samples in which this adjustment has not had an opportunity of taking place.

Dimensions of Test Pieces. With yarns and fabrics, when the

testing is carried out by the steady increase of the loading force, the rupture of each test piece takes place at the weakest point. With a given material, the greater the length of the test piece between the jaws, the higher the probability of the inclusion of points of subnormal strength. If therefore a value for the strength of a material is based upon the mean of a fixed number of single determinations, then the longer the test piece employed, the lower will be the mean value.

Number of Individual Determinations—Sampling Loose Fibres. Since all textile materials vary more or less in their point-to-point properties, an accurate representation of the properties of the material in bulk is obtained only by employing an efficient sampling system, and by making an adequate number of single determinations upon the representative sample thus obtained. Unfortunately it is not always possible to carry out the sampling procedure with the thoroughness necessary for obtaining a portion truly representative of the whole. For example, every cut made in a piece of woven cloth so seriously reduces its value that the removal of samples, for the purpose of control testing, from each piece of a batch of cloth undergoing processing, is often quite impracticable. Where, however, the material is in loose fibrous form, the system of sampling in operation for powdered solids can be followed. Handfuls of the material are taken at random throughout the batch, well mixed, spread out and divided into quarters. Two of these quarters are again mixed, spread out and again quartered, and so on until the selected sample is of conveniently small bulk. Since most fibrous materials are heterogeneous in size and are often in irregular aggregations, care must be taken that the quartering process does not bring about any selective separation of the varieties present, either by allowing the short fibres to shake out of the mass, or by a natural tendency to draw out the longer fibres. During the later stages of subdivision all aggregates present in the samples must be broken up.

Sampling Yarn. Where large batches of yarn have to be dealt with, there is usually little difficulty, since, with the exception of yarn in warps and on beams, the packages are small and numerous, and a number of these may be removed at random from the batch, and their number reduced by a succession of systematic divisions.

These sampling processes are appropriate only where the mean value of a limited number of determinations is intended to represent the properties of large quantities of material. Often an investigation of restricted portions of a material is necessary, and then the general methods of sampling outlined above are not appropriate. Even here, however, it is advisable to remove the test pieces from the restricted portion in such a manner that they are truly representative of this portion. In deciding upon the number of tests to be made on a given

sample, account must be taken of the variability of the material and of the magnitude of the experimental errors likely to be encountered in the single determinations. The more tests that are taken, the less will the mean value be influenced unfairly by abnormally high or abnormally low values among the individual determinations. Thus, let it be supposed that a number of separate groups of single thread strength determinations are carried out upon one sample of yarn, each group consisting of n determinations. If n is made very large the mean values for each group will coincide. To carry out a sufficiently large number of measurements to ensure that the mean has the same value however often the testing operation is carried out upon the same material, would be too laborious for practical purposes. Assuming that the variations in mechanical properties are distributed through the material at random, it can be shown by statistical methods that the probable divergence E_n of the mean of a group of n determinations from the true mean (which would be obtained by making n approach infinity) will be given by

$$E_n = \frac{\pm 1{\cdot}25\ D_n}{1{\cdot}48\sqrt{n-1}}$$

where n is the total number of determinations and

D_n is the sum $d_1+d_2+d_3\ .\ .\ .\ +dn$,

these being the respective differences between the values for the individual determinations and the mean M of the whole n values.

For example, in a yarn where D_n is found experimentally to be of the order of 20 per cent. of the mean value, a quite good figure for instance, for cotton yarns, then the percentage probable error of the mean is given as follows :—

No. of determinations.	E_n in per cent.
10	±5·6
20	±3·88
50	±2·42
100	±1·70
200	±1·20
500	±0·76
1000	±0·54

It will be seen here that increasing the number of observations much beyond 100 does not bring a corresponding advantage in the accuracy of the determination, since a change of 1 per cent. in the R.H. of the air could introduce errors of corresponding magnitude, and a difference of considerably more than 1 per cent. in the breaking strength of a cotton material could not be detected during the working up or wear of the material.

The application of this calculation to the results of tests on any

given material will furnish guidance as to the number of individual tests necessary. Without a knowledge of the circumstances, only very approximate information can be given. The number of tests necessary for cotton yarns ranges from 70 to 200. On the more regular rayons 20 to 50 will usually suffice. Tests on fabrics integrate to some extent the results of virtually a much larger number of single thread determinations, and therefore, unless there are obvious serious irregularities in the weave of the cloth, 10 to 20 determinations are sufficient.

Construction and Use of Testing Machines

The machines available for the testing of textile materials differ both in the important details of construction and in the subsidiary modifications of particular types of machine introduced by different makers. For this reason general critical treatment which may aid in the selection of a machine capable of carrying out tests with the greatest desirable accuracy in the shortest time and adapted most suitably to a particular kind of operator or for a particular range of work, will alone be attempted.

The machines adapted to the measurement of the strength and extension of single textile fibres such as those of cotton, wool, silk or rayon are much less frequently required than those which measure the strengths of yarns or cloths. They deal with loads of the order of a few grams weight and must be constructed with the accuracy of a chemical balance, while the mounting of the fibres and the operation of the apparatus calls usually for a certain amount of manipulative dexterity. On the other hand, testing of a material fibre by fibre is the only method available where the effects of, say, chemical treatment upon the mechanical properties of the fibre substance are required to be investigated. It has been considered advisable to mention only a selection of the principal fibre testers by name and, where possible, to give a reference to publications where further information may be obtained.

The earliest, and perhaps the simplest, is the apparatus of O'Neill,[1] and this machine has been improved by Mann and Pierce.[2] The fibre balance of Barrett [3] and the Deforden balance of Krais [4] are similar in principle, though in one the load is applied by electro-magnetic means and in the other by the collection of a stream of water in a container supported, via a balance beam, by the hair under test. Other machines are described by Matthews [5] and by Beadle and Stevens.[6] For the stronger fibres it has been found possible to adapt the machines of a design normally used for testing yarn (to be described

[1] *Mem. Manc. Lit. Phil. Soc.*, 1865, **2**, 389.
[2] *J. Text. Inst.*, 1926, **17**, 84 T.
[3] *J. Text. Inst.*, 1922, **13**, 17 T.
[4] *J. Text. Inst.*, 1928, **19**, 38 T.
[5] *Textile Fibres*, New York, 1926.
[6] *J. Soc. Dyers and Col.*, 1914, **30**, 94.

later in greater detail), and the firm of Schopper of Leipzig have done this. A method of testing the strength of small bundles of hairs when the stress is applied perpendicular to the hair axis is possible on the Amsler machine (*q.v.*). The bundle is cemented at both ends to a flat plate which is held horizontally in the lower jaw of the machine, while to the upper jaw is attached a smooth hook which is slipped under the bundle. When the jaws move apart the hair bundle is " plucked " by the hook at its middle and finally breaks. Where hair testing of cotton or other relatively weak fibres is a frequent occurrence, the Magazine Hair Tester of Balls [1] is very convenient. The machine is constructed by the Fine Spinners' and Doublers' Association of Manchester. A series of fifty hairs is mounted on a special holder and these are broken in succession by an automatic mechanism which records the strength of each hair. An autographic wool tension apparatus, which records the breaking load, the relation between the load and extension of the fibre, the extension hysteresis when a load short of breaking load is imposed and then removed, and other mechanical properties of the fibre, is constructed by the Cambridge Instrument Co. of London and Cambridge to the design of the British Research Association for the Woollen and Worsted Industries.

Considering the general requirements in yarn and cloth testing machines, a most important one, common to all types, is ease and rapidity in working. From what has been said earlier, it is evident that, since the number of tests required for a single sample may be of the order of one or two hundred, a machine which is cumbersome or slow in action will cause much waste of time and needless strain on the operator with consequent unreliable work. The jaws or clamps holding the test pieces, the levers whereby the machine is set in preparation for a new test, and any autographic recording mechanisms should all be within comfortable reach of an operator seated in front of the machine. Slight changes in the relative positions of these components may make surprising improvements in the ease of working, and it is recommended that practical trials of competitive instruments should be carried out before a final choice is made. A common type of dynamometer mechanism requires some device whereby the jaws or clamps holding the test piece are moved apart mechanically at a slow steady speed. The machine should be furnished with means for the rapid return of the jaws to their initial position at the conclusion of a test. There are still some machines in which the return of the jaws is brought about by putting the separating mechanism in reverse, so that the jaws are brought together at the same slow speed with which they were moved apart, and the time of carrying out a single test may almost be doubled.

[1] W. L. Balls, *Studies of Quality in Cotton*, London, 1928.

In many yarn-testing machines (where it is common for the test piece to be held vertically) the upper clamp or jaw is suspended at the end of a long flexible chain or steel strip and no guides are provided to hold the clamp steady when the end of the test piece is being inserted. This makes the operation of insertion unnecessarily clumsy and tedious, since both hands are required for tightening up the clamping arrangement. The clamp may thus prove elusive when working rapidly. Although this free suspension of the clamp obviates friction which is bound to be introduced by guides, there is no necessity for a long length of suspending chain. A further disadvantage is that transverse vibrations may be set up in the test yarn while it is being put under stress, with consequent interference with the regular applications of this stress.

The construction of the clamping jaws is also of importance. The surfaces which hold the yarn should be relatively large in area, the edges should be smooth, to avoid cutting or abrading the test piece at any time. The surfaces of the jaws should not be ridged, and, if they are lined with any slightly resilient material such as fibre composition, this material should be so hard that it is not scored by yarn being pulled through the jaws, as may happen when the jaws are not sufficiently tightly closed upon a test piece. The construction of the jaws should be so carried out that when the clamping force upon them is released, they stand open ready for the insertion of a new specimen. It should not be possible for yarn easily to get entangled in the jaws or to find its way into any hinges between them or into any other place where it can interfere with their operation. The jaws are commonly tightened either by means of a screw and milled nut, or by means of a cam and lever arrangement. The latter arrangement is the easier to operate, but it is not always adapted to a machine which has to deal with ranges of yarns of widely varying diameter. If it is fitted, it should be ascertained that the cam cannot slip or release its tension when the jaws are in the closed position. If the screw and milled nut are fitted, the boss of the nut should be fairly large in diameter and the projections of the milling should not be sharp, otherwise the fingers of the operator become cramped and sore at the ends.

It is self-evident that the quality of the construction should be high if accurate results are to be obtained. In the pendulum types of machine, the fulcrum should be as carefully made and as frictionless as possible. All the moving parts and framework should be solidly constructed so that reasonable use cannot cause warping or other maladjustment. Where springs are employed to apply the stress on the test piece, these should be of high quality steel, and the machine should be so designed that when they are exerting their maximum

intended tension, they are carrying at most one-third of the load necessary to extend them to their elastic limit. If, as is most usual, helical springs are employed, the compound spring, consisting of two springs, one within the other, the helix of the inner spring having the opposite direction of rotation from the outer, is very convenient, since by this means rotation of the spring as it is extending may be avoided. All types of plating are not equally satisfactory on springs, for instance chromium plating, unless carefully carried out, may soon strip in use; but some means of avoiding corrosion is necessary.

On many machines where the two sets of jaws are moved apart by an electric motor, the separating mechanism makes use of a threaded rod with a nut moving along it as it is rotated. Besides being cut with precision, this gearing should be stout in build, the thread should be sufficiently broad to minimize the possibility of distortion or stripping by an excessive load, and the rod should be so supported that it cannot bend at all as the load is taken up, otherwise wear of the thread causing backlash will result.

The length of a piece of yarn or cloth cannot be deemed to be measured accurately unless the tension conditions are also specified. When the piece is free it usually contains twist, curl or "crimp" which makes a point-to-point measurement inaccurate; if it is carrying an appreciable load the crimp will be straightened out, but there will be marked extension. It is therefore usual to measure the test piece when it is loaded sufficiently to straighten out the crimp, but insufficiently to cause marked extension. The magnitude of this load depends on the structure and extensibility of the material to be tested, but it is usually laid down that it should not exceed one-twentieth of the breaking load.

Since, as has been explained, the extensibility is usually measured at the same time as the breaking load, it is necessary that the length of the test piece should be of a fixed known value in each of a series of determinations. This is provided for by arranging that the upper and lower sets of jaws are at a fixed distance apart when the machine is set preliminary to making a test. (Many machines are constructed so that this distance may be altered. This is a useful feature, since some of the samples submitted to the testing laboratory may be too small for test pieces of the regular size to be taken.) The machine should also contain an arrangement for imposing the small stretching tension upon the test piece as it is inserted. This is often effected by allowing a slight freedom of vertical movement in the lower set of jaws, and the test piece is then inserted in such a way that it supports these jaws before any stress is applied by the testing machine, so that the weight of the jaws provides the necessary straightening load. This slight movement of the lower jaws is also made to actuate the

mechanism whereby the extension of the yarn is measured. On many machines this mechanism is one of the most unsatisfactory and erratically working features. When a machine is being selected, this part should be examined critically for convenience of setting, smoothness, and positive action.

If an autographic device for recording the stress-extensibility relationship of the test material is fitted (and this is strongly to be recommended, since much more complete information of the mechanical properties, construction, and history of the material is thereby made available), one or two features of the construction will require examination. It should be explained that the usual design of autographic device consists in fastening a piece of specially ruled graph paper round a drum or in a movable frame. By suitable connection with the testing mechanism the paper is displaced during a test in the direction of one of the ordinates to an extent proportional to the extension of the test piece, while a pen connected to the tensioning mechanism is displaced along the other ordinate by an amount proportional to the load. It will be found that the means of connection between the testing mechanism and the autographic recorder are not satisfactory in many machines. Cords or gut connections which are often employed do not retain a constant length through fluctuating atmospheric humidities, and fray readily through wear. In many machines these cords are guided by pulleys the grooves of which are too shallow so that the cords tend to slip off while the testing machine is in action. The pens used on many of the autographic devices are the source of much exasperation. The pen itself should be capable of adjustment on the end of its lever so that a very light contact with the paper may be obtained. The pen should not be so constructed that evaporation of the ink supply is encouraged, or that the flow channels block readily (systematic cleaning of the pen, and the use of a good quality recording ink will contribute to its satisfactory behaviour). The supply of ink to the pen point, while not being excessive, should be reasonably copious, otherwise rapid movements of the recording lever will not be registered. The lever holding the pen should be so constructed that the pen-point may be moved out of contact with the paper except when a record is being made, otherwise the records will be embellished with meaningless lines as the preliminary operations of the test are carried out. Some means should be arranged for damping vibration of the pen lever when the test piece breaks as this often results in blots of ink being thrown over the record.

One of the most convenient types of recording device is attached to the Balls' magazine hair tester mentioned above. Here the pen is replaced by an insulated needle with its point fixed a few milli-

metres away from the paper record. The needle is connected with one lead from the secondary of a small induction coil, the other lead being connected to the metal plate which supports the paper. A trace is burnt in the paper by the sparks passing between the needle and the paper. This arrangement gives clear records and there is no friction at the paper surface.

Motive Power. With the exception of machines of the rarely encountered Krais type where the load is applied by water running into a container, or of the Avery cloth-tester type where a stream of lead shot provides the increasing load, or the recent Scott inclined plane tester,[1] most machines operate, as has been stated, by the steady separation of the jaws holding the test piece. This movement is commonly effected in one of four ways: (*a*) By turning a hand wheel; (*b*) by drive from an individual electric motor, or belt or chain connection with a countershaft driving other machinery; (*c*) by gravity, a weight attached to, or mechanically connected with, one of the jaws being lifted by hand when the machine is being prepared for a test, and being then allowed to fall, its movement being controlled by a piston working in a cylinder filled with oil or some viscous fluid; (*d*) by a piston actuated by a flow of water from the mains.

Of these four types: (*a*) is not normally to be recommended, since it requires practice to maintain a constant speed of operation, uninfluenced by what is seen to be happening to the test piece. It is fatiguing to the operator. Only in heavy machines where occasional tests are required, and the cost of power-operated apparatus is not warranted, and where also the methods (*c*) to (*d*) are not practicable, may its use be justified.

(*b*) This class of drive is most to be recommended. Usually, specially constructed motors are included by the makers of testing machinery. These are slow running, shunt wound, and are connected with the apparatus through a clutch and worm reduction gear (or threaded rod and travelling nut). Such motors will remain constant in speed through considerable fluctuations in load. It is advisable to arrange that the motor runs continuously during the whole period of use, the testing apparatus being started and stopped by means of a clutch mechanism, rather than by starting or stopping the motor itself. This applies with less force to light yarn testers actuated by small high-speed motors with a high-ratio reduction gear. As the motor may run almost continuously for many hours in the day, it is advisable to see that it is rated generously for continuous running. The drive from counter shafting, operating other machinery, is fairly common in mill spinning rooms, etc. As, owing to the large speed reduction, the load on the driving belt is not usually great, little

[1] Hunter, *Rayon Textile Monthly*, 1936, 17, 739, 805.

trouble due to slippage is encountered if the belt is maintained in reasonably good condition. It is, of course, necessary to drive from shafting which runs at a reasonably constant speed, a 10 per cent. variation being the maximum permissible.

(*c*) A large number of machines incorporate the oil-controlled, gravity-operated mechanism. It is reasonably satisfactory for practical purposes, has the advantages of enabling a self-contained and portable machine to be built, and does not readily get out of order. The use is limited for the most part to single-thread testing machines where the maximum load to be applied is not high, since, for heavy machines, the necessity to lift a large weight between each test requires a good deal in strength and endurance from the operator. In many machines the piston fits tightly in a vertical cylinder, and in the downward movement the oil displaced from the lower side of the piston escapes through a small orifice in the piston to the upper side. A clack valve, or cup-shaped packing to the piston allows the oil to escape rapidly to the lower side when the weight is lifted to reset the machine. It is advisable to see that the size of the small orifice may be varied by fitting a needle valve or some such device in order that the speed of the piston may be adjusted as required. A return valve is preferable to the use of cup-shaped packing on the piston. A good quality light oil should be used, and it should be changed from time to time. All leather washers and packing material should receive periodical overhaul. The speed of the piston will, of course, be affected by alteration in the oil viscosity, and as heat is developed by friction during the course of operation, and as oil has a higher resistance to shear after standing, the weight should be lifted and allowed to fall a number of times before working on a machine that has not been in use for some time, in order that the normal working viscosity of the oil may be acquired. If the temperature of the testing room should depart widely from the normal, the speed should be checked and, if necessary, adjusted by means of the orifice valve.

(*d*) The machines operated by mains water pressure are not now much in evidence. They suffer from two principal disadvantages. First, mains water pressure is often very variable, particularly in works where large quantities of process water may be used, and, secondly, the return of the piston after a test has been made is usually effected by means of a valve which causes the water pressure to be applied on the opposite side of the piston from that to which it is applied when the test piece is being put under load. As the speed of traverse of the piston is usually adjusted by passing the water from the supply through a needle valve before it enters the cylinder, this means that the return movement of the piston is restricted practically to the same speed as that necessary for the test proper, and the time of a single complete testing operation may be inconveniently long.

A widely adopted pattern which is utilized in machines over a large range of capacities is the weighted pendulum machine shown in diagram in Fig. 129.

The test piece P is held between jaws J1 and J2. J1 is suitably

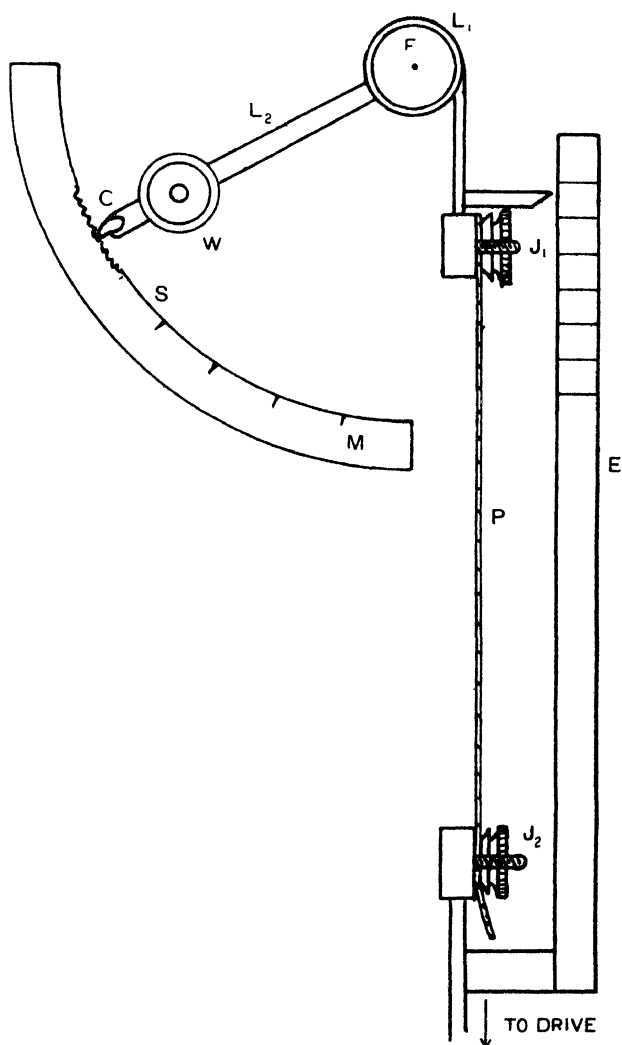



FIG. 129.

attached to the short arm L1 of a lever, pivotted at F. The longer arm L2 is weighted at W. At the end of L2 a pawl C engages in ratchet teeth cut in a bar S. The toothed edge of S forms part of a circle with the centre at F and the radius of length L2. Thus, after L2 has been displaced by the force transmitted by P, it cannot fall back

when P breaks. On the surface of S is marked a scale M showing the displacement of L2, and calibrated directly to indicate the load exerted on P. During a test the jaw J2 is moved downward at uniform speed by one of the mechanisms described above. The extension at break is measured by a scale E which moves downward with J2, while P is intact, and, in conjunction with a pointer attached to J1, shows how far the original distance between the jaws (the original length P) has increased during the test. This arrangement cannot give a uniform rate of loading, firstly, because equal angular displacements of L2 correspond to much smaller increments of load when L2 is near its vertical position than when it is near its horizontal position, and secondly, because P does not extend under load at a uniform rate. However, for many types of testing, machines of this construction are adequate, and are very convenient in use. Messrs Goodbrand have introduced a machine for yarn testing in which the first disadvantage is obviated by a modification of the single pendulum arrangement so that equal increments of load correspond to equal scale displacements over the whole testing range. It should be mentioned that, on many of these machines, the weight W may be augmented by the addition of one or more extra attachable weights, so giving the machine more than one testing range. There is then, of course, more than one scale required on S, parallel scales, each corresponding to one of the respective weights of W, being provided. Makers of machines of this type include Goodbrand and Cook, both of Manchester, Schopper of Leipzig, and Baer of Zurich, and the same principle is applied to machines ranging in capacity from those testing fine counts of cotton yarn or bundles of fibres to those testing broad strips of heavy canvas duck.

In the spring type of machine, including the Muller-Leuner, the Amsler and the Shorter-Hall (made by Reynolds and Branson of Leeds), the general details of construction are similar in their main outline to those of Fig. 129, except that J1 is now attached to one end of a spring the other end of which is held stationary. As J1 is pulled down by P, the spring is extended and so exerts a proportionally increasing tension on P. A pointer and scale, or a connection with a recording arrangement calibrated in terms of the tension exerted, indicates this displacement. The springs may be of the spiral type as in the Amsler machine and a series of interchangeable springs is generally provided, since the range of tensions which a single spring can exert, under correct conditions of working, is not very large. In the Shorter-Hall machine the tension is provided by the bending of a length of springy strip held at one end, and connected with J1 at the other. The range of tensions in this machine is varied by changing the effective length of the spring. Unfortunately the general construction of this machine is cumbersome.

Owing to the absence of regular extension in yarns and fibres as they are put under load, the tension does not increase regularly or uniformly on successive test pieces, even though the displacement speed of J2 remains constant. This difficulty has been recognized for some time and various methods have been devised to overcome it, and though a number of machines have been constructed embodying these devices, they are, on account either of the greater complexity of design or the somewhat greater difficulty of operation, not so generally popular as the simple pendulum or spring machines. In the simplest, one of the jaws is attached to one arm of a beam balance. To the other arm of the balance is attached a container, suitably counterpoised. A steadily increasing load is obtained by running water, sand, lead shot, etc., through a small orifice in a steady stream into the container. The lower jaw is attached to a mechanism, usually operable by hand, by which the jaw can be lowered as the test piece extends. This is so operated that it takes up the extension in the test piece as it is produced so that the beam remains horizontal during the test. When the test piece breaks it can no longer maintain the beam in a horizontal position, and this is pulled over by the weight of shot or water. In doing so, it actuates a valve which cuts off the supply of loading material. On the heavy machines, when lead shot is employed, the weight of shot required is read off directly on a spring balance which is interposed between the container and the beam. On the fine balances (*e.g.* Krais balance) the weight of water is estimated either by an independent weighing, or by suitably measuring the volume of liquid.

A modification of the constant-loading design, designed to take heavy cloths and also used extensively in tensile testing of metallurgical specimens, uses a heavy trolley of known weight which is made to exert an increasing moment on the longer arm of the beam by being moved at a uniform rate along this arm from the fulcrum to the outer end. In this machine, too, the extension of the test piece is taken up by moving down the lower jaw by a hand device. This principle of the mechanically actuated steel yard is also embodied in a yarn balance designed by Dr Schultz of B.I.S.F.A. Here a weight is moved along the beam by the rotation of a threaded rod, and the displacement of the weight (recording the load) and the displacement of the beam (recording the extension) are drawn automatically on graph paper with rectangular co-ordinates. The manual adjustment of the jaws may be replaced by mechanical or electrical arrangements which automatically adjust the distance apart of the jaws as the test piece extends. Their action is controlled from the beam, and they are set in motion when the beam departs from the horizontal by more

than a predetermined amount. H. Cliff[1] has described a very ingenious design for a uniform loading strength tester for yarns, particularly rayon yarns. The machine records the load-extension curve.

In the so-called ballistic yarn and cloth tester, the conditions of testing are very different from those just described. Here the breaking load is applied by impact and the material has little time for structural adjustments during the sudden rupture. As a result the value obtained is more nearly a summation of the strengths of the constituent fibres at the point of rupture. The value for breaking load obtained by the impact method may represent more nearly the reaction of the material under test to the sudden stresses of wearing and other processes to which it may be subjected. The mode of action of the ballistic tester has been investigated by Lester[2] and a convenient machine has been manufactured by Goodbrand. This consists of a weighted pendulum, which at the beginning of the experiment is held in a horizontal position by means of a catch. The test piece is attached at one end to the end of the pendulum and at the other to a fixed clamp. The position of this clamp and the length of the test piece are so arranged that, when the pendulum is released, the test piece is in a horizontal position and is taking the stress when the pendulum bob is at its lowest point. The work of rupture is measured by allowing the pendulum first to fall freely, and then with the test piece attached and noting the diminution in amplitude caused by the attachment of the test piece. In actual practice the resistance to rupture of the sample is read off on a scale by means of a light pointer which shows the amplitude of the swing. The ballistic tester is rapid in action, simple to operate, and it can be arranged to test yarn in the single thread and in the lea hank, as well as testing strips of cloth. It is claimed that the strength returned by this method is not the strength of the weakest point of the test piece but of the whole span.

For carrying out single thread tests where large numbers of individual tests are required, *e.g.* in extended work on the effects of chemical treatment, in evaluating cottons by spinning tests, or in carrying out continuous control tests on yarn during their manufacture or processing, the Moscrop automatic tester has many attractive features. Six samples of yarn from bobbins, cops, hanks, etc., may be led into the machine which may then be started and which will continue to operate until it has made eighty breaking tests upon each sample. Breaking load and extension at break are automatically recorded, and the individual results are separated on the record into groups according to their magnitude, thus facilitating statistical

[1] *J. Text. Inst.*, 1933, **24**, T 351. [2] *J. Text. Inst.*, 1910, **1**, 63.

treatment. In this way reliable figures for the regularity of the yarn are easily obtained. The ability to test six samples simultaneously is of great value in chemical investigations where six samples of the same yarn which have undergone different treatments may be tested under identical conditions of humidity.

Primarily, with the object of reducing the large number of determinations necessary for obtaining a reliable mean value of the single thread strength, the so-called lea test is often employed. In this test a length of 120 yards of yarn is wound into a hank of 54 in. girth on a special wrap reel. This hank is then removed and broken in a machine in which the jaws necessary for yarn and cloth are replaced by smooth hooks over which the hank is passed. Although the strands of the hank can move relatively to each other at the beginning of the test, as the load is increased there is a tendency for them to become clamped at the hooks by their mutual pressure. For this reason the strands which are least extensible must take the load first, break, and thus throw a larger proportion of the load on the remaining strands. A yarn in which the extensibility is uneven tends to show a low lea strength as compared with a yarn whose mean strength may be less but which may be more regular in extensibility. Therefore the lea test gives a value which is connected not only with the average single thread strength but also with the regularity of the yarn.

As has been indicated already, the testing of cloth, by breaking strips of it between jaws by a stress applied parallel to its surface, does not differ in any essential respect from the determination of the single thread strength of yarn but requires only suitably designed jaws and, in general, a more robust testing machine. The bursting test by such machines as the Mullen or Schopper is, however, different in principle. Here a portion of the surface of the sample is clamped between two annular clamps each of the same dimensions, and arranged so that the central holes in top and bottom clamps coincide. To the underside of the circle of cloth thus surrounded by the clamps a stress is applied at right angles to the cloth surface. This is effected through a rubber diaphragm which presses against the underside of the cloth, and which forms one face of a capsule connected with a hand-operated pump. Glycerine or other liquid is forced by the pump into the capsule expanding the diaphragm against the clamped circle of cloth and causing it ultimately to burst. A manometer shows the pressure exerted by the liquid at the bursting point. Unless it is known that only light cloths are to be tested it is advisable to obtain a pattern of bursting tester on which the maximum recommended load is fairly high. If a small model is obtained, and worked continuously up to, or over its capacity, frequent bursts in the diaphragm

may be experienced. The bursting tester is of particular value where relatively small samples of cloth, probably cut square, are submitted and it is difficult to cut representative warp- and weft-wise strips. It is also valuable for exploring the point-to-point variations in strength in samples which are suspected of having suffered local degradation.

General Precautions in carrying out Tensile Tests. These precautions are based for the most part on the necessity of disturbing the original condition of the samples as little as possible and for introducing no accidental factor which would cause the measured value to be an inaccurate reflection of the true properties of the material.

In all types of testing, it should be made a principle to avoid handling the sample unnecessarily, and to avoid completely the handling of that portion of the sample which will come between the clamps or jaws of the testing machine. The hands may impart moisture, or grease, or may warm up the sample and so produce an accidental local change in the original properties. Sufficient abrasion to produce a weak spot may often be difficult to avoid when preparing certain types of yarn or cloth for testing. In single thread testing the yarn should be unreeled slowly from bobbin, cop or hank, avoiding jerking and never allowing a hard-twisted yarn to become so slack that extensive snarling can take place. In most yarns, but particularly with hard-spun or hard-twisted yarns, there is a tendency for the yarn to untwist at a cut or broken end. For this reason a test piece should always be sufficiently long to allow an adequate distance between the cut ends and the clamped portion so that no partially untwisted material is included between the jaws of the testing machine. When crepe yarns are being dissected from cloth, it is advisable to fetch out one end of the length of yarn, holding it to prevent untwisting until it can be fixed in the clamp, and then to withdraw the rest of the length from the cloth and hold it so that no untwisting can occur until the second clamp has been tightened upon it. In fixing yarn into the testing machine all tendency to overstretch it should be avoided, and with wet rayon this requires special care. The handling of rayon must be very gentle, as filaments are readily broken, and if the skin of the finger-tips is hard and rough there is a risk of damage to the sample, which may be minimized by washing the hands and then rubbing into the skin a little lanoline or similar preparation.

Yarns and cloths should be secured in the clamps or jaws so that they cannot slip when the load is applied. If this slippage is considerable, it is, of course, readily detected, and the result of the determination will be discarded, but if the slippage is relatively slight, it may only be indicated by an abnormally high extension. In the event of a high extension being recorded it is advisable to test for slippage by pulling

at the broken fragments of the test piece before the clamps are loosened. The results of a breaking test on yarn that has been already under tension in the machine, are quite worthless and in taking successive test lengths from a continuous yarn sample it is essential to see that yarn which has been under stretch or has been between the jaws during one test is not included in the succeeding one. Where local chemical attack on the yarn is being investigated, the broken portions of any test piece that shows low strength should be preserved. The ruptured ends are tied together in a knot so that they may later be found and subjected to chemical test.

In lea testing it is essential to have a good, well-made wrap reel. If the sample is in the form of a hank, it pays to shake it out carefully and to place it with as little disturbance as possible on a well-made collapsible swift which can rotate smoothly in a suitable stand. The tieband may then be cut, the correct end found (making sure to tie the remaining end to the swift so that it shall not lash about) and a few yards pulled off until it is quite certain that the yarn will wind smoothly from the swift. In choosing swifts for supporting the yarn samples, those which have cord supports for the hank, and those in which the yarn is supported over a couple of squirrel's cages should both be avoided. When winding off lea hanks the wrap reel should be started slowly and then rotated at a uniform rate until almost the required length has been reeled. The wrap reel may then be run more slowly until the correct length of yarn has been taken up. Then the two ends of the wound yarn should be brought together without stretching and tied together by six reef knots. The lea hank should be removed from the wrap reel very carefully, sliding the hank a short distance at a time along successive ribs round the circumference of the reel, and repeating until the hank is at the edge of the reel. It should then be taken off, supported on the index finger of each hand in such a way that the parallel disposition of the strands composing the hank is not disturbed and placed with as little disturbance as possible upon the hooks of the testing machine. Since the lea hank represents an accurately measured length of the yarn, it is convenient to measure the count by weighing the broken leas (7 leas = 1 hank):—

$$\text{Count} = \frac{1 \text{ lb. or } 543 \text{ g.}}{\text{weight of 1 hank}}.$$

In testing cloth by breaking strips cut in the direction of the warp or weft of the piece, some care must be exercised in the preparation of the strips. These should, if possible, be at least twice as long as the standard test length. They must be prepared of a standard width which varies with the type of machine in use. The strips should never be torn but should be cut with a razor-blade, using a metal

ruler as guide, having previously laid the cloth out flat and made sure that warp and weft are reasonably straight and perpendicularly disposed. It is advantageous to cut the strips slightly wider than is required, pulling out yarn from the cut edges on either side until the correct width is reached. In putting these strips into the jaws of the testing machine, care should be taken that they sit squarely in the jaws. If very light materials such as voiles are too thin to be held securely by the jaws of certain types of machine, packing with one or two thicknesses of a heavier cloth will be of assistance. In certain machines which take narrow strips and in which the construction of the jaws prevents the insertion of the test piece from the side, *i.e.* where the end of the test piece has to be threaded directly between the opened jaws, it is of assistance to shape the end of the test piece in the form of a point by means of an oblique cut. Flimsy materials are conveniently cut in a large print trimmer or with long sharp shears, after placing the cloth between two stout sheets of paper.

In operating a bursting tester, it is very important to see that the cloth is firmly clamped in the machine. Inspection of a machine like the Mullen tester will show that a considerable area of the sample is compressed between the clamps. This area should not, unless paucity of testing material renders it imperative, be included within the bursting area during a subsequent test. It is, of course, important that all creases or wrinkles be smoothed out of the cloth before it is clamped in the testing machine.

V. CHEMICAL TESTS ON TEXTILE MATERIALS

By H. A. TURNER, M.Sc., A.I.C.

Apart from the tests for the identification of the textile fibre, the majority of the chemical tests in use are tests of the quality of the fibrous material from which the textile is made. They are, for the most part, devised to show, qualitatively or quantitatively, the chemical changes which have taken place in the material since it was obtained in the raw state. During the bleaching, dyeing, printing and finishing processes, and during use and wear of the material, changes may be introduced into its chemical structure. These changes are reflected, and may be observed, as changes in the physical or physico-chemical properties. One of the commonest is a loss of strength and durability. Another is a modification of dyeing affinity, and this is particularly obvious when the cause has operated unevenly over the area of the textile, so that fabric which should normally dye evenly comes from the dyeing process with some areas dyed more deeply than others.

Often the purely chemical effects can be imitated very closely by

purely mechanical effects. When a material has an unexpectedly low resistance to wear, it may be difficult to decide from a visual inspection whether this has been caused by some change brought about in the chemical structure of the material, or whether prior mechanical influences like abrasion have been at work. Local differences in the appearance of a dyed material may be due to changes in the affinity of some areas brought about by the irregular action of chemical reagents, to the imperfect application of the colouring matter, to differences in structure of the yarn or to irregularities in the weave of the cloth which owe nothing to any chemical changes.

In general, it may be said that weakening of textile structures due to mechanical degradation, or irregularities in their appearance due to faulty arrangement of the component structural units, are not accompanied by any change in the chemical structure of the fibrous material. For this reason it is mostly possible by the application of the appropriate chemical tests, by the combination of these tests with an examination under the microscope, or by the application of certain of the common mechanical tests, to decide whether faulty behaviour or appearance has a chemical or a mechanical origin.

This question is perhaps more important in England than in other countries owing to the division of the textile industry, so that spinning, weaving, and chemical processing are mostly carried out by separate firms. Often faults which have been produced in the early stages of manufacture become apparent only in the later stages or after the goods have been sold, and the responsibility for their production may be disputed by each of the different firms which have had a hand in the fabrication of the goods. In these circumstances, a careful investigation may be called for, and it is often possible, by the appropriate tests, to establish the incidence of the fault.

The technique of chemical testing, as is natural from the greater diversity in the chemical structure, differs greatly according as the textile material is of animal or of vegetable origin. But some generalization may be attempted, and it may be said that the chemical causes of faults may, for the most part, be grouped into four large classes : the modifying action of excessive heating, the action of acids, the action of alkalies and the action of oxidizing agents. The general history, from a chemical point of view, of the goods may often be inferred from a consideration of their appearance and finish, and it may then only be necessary to refer the cause of the fault to one of the four classes mentioned above in order to decide at which stage in the manufacture it was produced.

The investigation of chemical modification of the fibre has reached a higher state of precision and usefulness in the vegetable group than in the animal group, though even in the former it is not satisfactorily

comprehensive. When dealing with defects in processed materials one of the great difficulties is that often the unprocessed material is not available for examination at the same time, and this demands an absolute significance from the results of the tests which is unobtainable. Another difficulty is that the tests for chemical degradation of a textile material often depend upon the recognition or estimation of the degradation products. These may have been removed by chemical processes subsequent to the one in which the damage was caused. When the processing of the material is shared between a number of firms, it is obviously impossible for one of them to demand that samples of the material be retained at each stage of the manufacture, but when the processes are all carried out under the same roof, and extensive routine testing is used to check the efficiencies of the different departments, a more systematic retention of such samples is often possible.

Before applying the more elaborate tests, much information may often be obtained by a careful inspection of the samples submitted. If weakness is complained of, it should be ascertained if the material is uniformly below strength, or if weak places only are present. If the material is not uniformly weak, it should be ascertained if the faulty areas are distributed entirely at random, or if they are spaced regularly according to some periodic pattern. In a woven fabric it should be ascertained whether the whole of the yarn at a weak place has been affected, or if the damage is confined to one set of yarns only so that it must have occurred before weaving. It should be noted whether staining accompanies the fault. If it does, the stain should be examined for the presence of metals. Examination of the material in the light from an ultra-violet lamp often shows up stains that are not normally visible. If irregularities of colouring are complained of, similar note of the distribution of the faulty places should be taken. The shape of the faulty areas in cloth is often significant, and it should be noted whether they are spots, round patches, splashes, smears running warpwise, smears running weftwise, bars defined by the weave of the material, etc.

Stripping and Re-dyeing

When investigating examples of irregular dyeing on textile materials, one of the first operations necessary may be the removal of the dye. If this is followed by re-dyeing with a dye or mixture of dyes which is sensitive to changes in the intrinsic dyeing properties of the fibrous material, it may be ascertained if the irregular distribution of colour is due to some irregularity in the properties of the material itself, or is due only to the imperfect application of the dyestuff during the dyeing process. In the former, the fault will be reproduced on re-dyeing,

whereas in the latter an even dyeing will be obtained. With the exercise of caution in the interpretation, the principle of stripping and re-dyeing can be extended. For instance, it may be of value, in investigating a fabric or yarn in which irregular dyeing properties are suspected to be due to irregularities of mercerization, to remove the original dye, stretch the material on a suitable frame and remercerize before re-dyeing. Where the fault is not due to faulty mercerization, but is due, for instance, to some defects in the structure of the yarn, the remercerization treatment will probably not eliminate the unevenness.

Stripping.—In carrying out stripping experiments, the removal of the dye is not the only consideration. The chemical treatment must not be so severe as to remove chemical evidence, nor must it produce modification of the fibre-substance on its own account. As an example, a preliminary examination may suggest that patches of light-dyeing material on a bleached cotton cloth are due to local excessive oxidation of the cellulose. It may be decided that an appropriate test to apply is the copper number (see p. 716), which depends upon the measurement of the reducing properties of the oxidized cellulose. If, however, the material has previously been stripped of its dye by the use of a hot, alkaline solution of a reducing agent, the results of the copper number test will be meaningless, since alkalis decompose and remove the reducing oxidation products of cellulose. Dyes of many classes may be partially or wholly decolorised, if not removed, by oxidizing agents such as hypochlorites. As there is always a risk that oxidizing agents of the strength necessary to decolorise dyestuffs will also modify the fibre and, so to speak, cause a swamping of the original fault, their use for stripping purposes prior to chemical tests should, where possible, be avoided.

Stripping prior to re-dyeing should mean the removal of the dyestuff and everything connected with it from the fibre, and not the mere decolorisation of the fabric. Decomposition products of the dye left on the fibre may act as mordants in the re-dyeing processes. If the original dye has been applied on mordanted material, or if after-treatments with metallic salts have been employed, care should be taken to remove the mordant or the metallic residue, as well as the dyestuff.

Many direct dyestuffs may be removed from the fibre by treatment with hot (80°) solutions of hydrosulphite of soda. The hydrosulphite is usually more effective when used without the addition of caustic soda. If the solution is brought to the boil, the hydrosulphite decomposes too rapidly to have much effect. The addition of sodium bicarbonate to the solution will delay the deposition of sulphur. The hydrosulphite should be used fairly strong (5 per cent.), and if the

reduction products of the dyestuff are retained tenaciously by the material, the addition of 10 per cent. of a solvent such as pyridine or ethylene-glycol mono-ethyl ether to the hydrosulphite solution will assist in their removal. The addition of powerful cation-active dispersing agents such as the Lissolamine A of Imperial Chemical Industries will also accelerate the stripping. Many direct dyes can be removed completely from cellulosic materials by repeated extraction with aqueous 20 per cent. pyridine, used warm, and this method is less likely to cause interference with the chemical properties of the cellulose.

Aniline black can be removed only by repeated alternate treatments with hydrosulphite and acidified hypochlorite used warm. The latter reagent is most effective if the material, after reduction to the brown leuco-compound with hydrosulphite, is plunged at once into boiling water, to which are added successive small doses of a 5° Tw. hypochlorite liquor, boiling up again after each addition. Care should be taken that the tendering which is inevitable in such a process, does not become excessive. This method is appropriate for stripping prior to the Ermen mercerization test since a moderate degree of degradation of the cotton will not interfere with the test.

The stripping of acetate colours from ester rayons is often relatively easy. Bleaching out the colour with slightly acidified chemic, a method frequently employed in the works for bringing down incorrect shades, should obviously be avoided. Besides bringing in the risk of further degradation of the cotton, it has the disadvantage that it does not remove all the acetate colours but turns a few of them into very resistant coloured products. Sometimes the method of treating with a hot soap bath containing 1 to 2 per cent. of a finely divided active carbon, such as carboraffin, will reduce pale shades to a sufficient degree for the purposes of re-dyeing. If, however, small pieces of the dyeing only are to be treated, solvent extraction of the dyestuff is to be recommended. Most of the acetate colours may be removed from the fibre by repeated extraction with warm ethyl alcohol. The temperature should not exceed 50° and the piece should not be allowed to crease or wrinkle during treatment. It is best to carry out the extraction in a large basin heated over a water-bath, so that the sample being extracted can lie flat at the bottom. A better method is to carry out the extraction cold, adding to the alcohol a limited proportion of a solvent for cellulose acetate. The latter solvent should be present only in such proportions that incipient swelling of the acetate takes place, for instance, 20 per cent. of acetone in the alcohol is very effective. The sample should be soaped at a moderate temperature with a solution of neutral soap before re-dyeing.

Basic dyestuffs are removed from cellulose fibres by extraction

with alcohol in much the same way as acetate colours are stripped. Not all the basic dyes are amenable to this treatment. The metallic portion of the fixing salts can be removed by steeping the stripped material in cold 5 per cent. hydrochloric acid, followed by thorough washing.

Vat colours are stripped by repeated extraction with warm alkaline hydrosulphite containing 20 per cent. of pyridine. Excess of alkali makes the stripping action more difficult. A useful procedure is to make up a plain 2 per cent. sodium hydrosulphite, place in it a small strip of cotton cloth dyed with Caledon Jade Green and add cautiously a solution of sodium hydroxide until the reddish-purple of the free leuco-compound of the dye is changed to blue. An effective but expensive method is extraction of the vat dye with molten phenol, cresol or resorcinol.

Re-dyeing of Stripped Samples.—The re-dyeing of faulty material should first be carried out with a dye which is especially sensitive to the kind of fault suspected. Later, if desired, dyeing can be carried out with more normal or better levelling dyestuffs to assess the seriousness of the fault from a technical point of view. Generally speaking, for cellulosic materials the same kind of fault in the material will have the same effect on the uptake of direct, vat, sulphur and the more substantive of the Naphthol AS or Brenthol products. Therefore re-dyeing with a direct dyestuff will often serve to distinguish between faults in the application of the dye and faults in the material for samples dyed originally with any of these classes of colour. A fairly sharp distinction may be made between those faults which derive from local inconsistencies in the degree of dispersion or orientation of the fibre substance, *e.g.* differences of mercerization in cellulosic materials, and those faults which arise from irregularities in the chemical properties, *e.g.* local over-oxidation. For cellulosic materials, probably the most sensitive single dye for the former class of fault is Sky Blue FF. It should be applied from dilute solutions, without any addition of salt, to obtain the maximum differentiating effect, and with the bath temperature not too high, *e.g.* not exceeding 60°. Irregularities in the absorption of the cellulose will then be shown up by differences in the depth of the dyeing. Often, however, local differences in the dyeing properties of textile materials are more perceptible if they appear not as differences in depth of colour but as differences in hue. For this reason mixtures of dyestuffs are often suggested for re-dyeing. One at least of the dyes should be sensitive to the fault under examination, and another of the component dyes should be relatively insensitive and should be of a contrasting colour. An example of such a mixture is the one recommended by the Shirley Institute [1] which contains 0·71 per cent. of commercial Sky Blue FF, 0·17 per cent. of Chlorazol Fast Red K and 0·13 per cent. of Chlorazol

[1] Clibbens and Geake, *J. Text. Inst.*, 1933, **24**, T 266.

Yellow BN. On ordinary cotton, this mixture dyes a neutral grey, but as the degree of mercerization is increased the proportion of blue taken up by the material increases and the dyeing is of a much bluer shade. Many of the sulphur dyes are particularly sensitive to differences in the mercerization of cellulose, one such dye being Thional Brown R. Differences in the chemical properties of cellulose, such as affect its affinity for direct dyestuffs, are shown up very readily by dyeing with Erika Pink B. J. Lomax has found that acid dyes along with direct dyes often give mixtures which are specially sensitive to local over-oxidation of cellulosic materials. The following mixture is very effective; it is actually used for dyeing silk hose with cotton tops, and if the tops are made from yarn which has patches of overbleached cellulose, the results with the direct dye components of the mixture are reasonably level, but very uneven effects are produced as soon as the acid colours are added. The mixture is :—

0·3 per cent. Chlorazol Brown LFS
0·05 ,, Chlorazol Fast Orange AGS
0·08 ,, Cloth Red GS
0·09 ,, Coomassie Navy Blue 2RNS
0·36 ,, Citronine YS

calculated on the weight of the goods.

The detection of resistant materials of a fatty or oily nature which cause light patches during dyeing with direct or similar dyestuffs can often be detected by dyeing with dyes which possess marked staining properties for hydrocarbon materials. For instance, to detect traces of linseed oil sizes on rayon warps, Böhme recommends the use of Sudan Red 7B or of the well-known Sudan III. The dye is suspended in 10 parts of methyl alcohol and the suspension is stirred into 100 parts of cold water. The sample is placed in this suspension for three minutes and is then washed for ten minutes in running water. An alternative which may be more convenient is to dye the material in the ordinary manner in a dilute bath of S.R.A. Red III or S.R.A. Blue III. These tests, while not so sensitive as the Osmic acid test (see p. 669) will often deal satisfactorily with concentrations of oil on the fibre which cause perceptible unevenness with direct dyes.

Tests for the Chemical Degradation of Cellulose

The tests group themselves into three classes as depending on :

(*a*) The development of reducing properties in the material as a result of the degradation.
(*b*) The formation of carboxyl groups in the degraded cellulose.
(*c*) The detection of the shortening of the chain molecules of the cellulose as the result of chemical action.

Reducing Properties of Modified Cellulose.—Qualitative tests usually consist in treating the material with a reagent which will provide on reduction a coloured deposit on the affected portion of the fabric or yarn. They are thus often of great value in defining the shape and size of the affected portions in cases of local chemical attack. They are of less value when a uniform degradation of the material has taken place, unless some of the original unprocessed material is available, or else a series of samples of a similar material which have been degraded by different known amounts. For determining whether a known material has received excessively severe treatment during processing, one of the quantitative methods is to be preferred. The tests which depend on the detection of abnormal reducing powers in the material have only a limited value for universal application, since they also respond to reducing impurities not derived from the cellulose itself. Further, the treatment of degraded cellulose with alkaline solutions, even under relatively mild conditions, decomposes or removes the reducing degradation products. These facts render it necessary to exercise caution in interpreting the results of tests for modified reducing cellulose, and make it essential to carry out careful control experiments or to consider the results in the light of the known or probable history of the material.

In all quantitative tests, whether for reducing properties or not, the material must be freed from size and finishing matters, and, in certain cases, dyestuffs on the fibre must be removed. These preliminary operations must be carried out so as to induce no fresh degradation in the material, and, where the reducing properties are being tested, the purification must not be carried out with alkaline solutions. Enzyme desizing with such preparations as Diastafor, Novo Fermasol, Rapidase (Rapidase F is a proteolytic desizing agent for the removal of protein-sizing materials), etc., are carried out at the concentrations and temperatures recommended by the makers, and it is specially important to follow the desizing treatment with a number of washes with hot water to remove the degradation products. Where it is suspected that oily impurities are present the preliminary cleansing treatment can be carried out with one of the new detergent preparations containing an organic solvent such as Astol A (I.C.I.), Imerol L (Sandoz), Lanaclarin (Böhme), etc. As an alternative, the sample may be saturated with oleic acid, allowed to stand for a short period and then treated repeatedly with warm dilute ammonia solution, followed by thorough washing with hot water.

Many of the methods for the estimation of the reducing power of degraded cellulose involve the reduction of a compound of a metal from a higher to a lower state of oxidation. Most of these reductions require to take place in alkaline solution where the reducing power

of carbohydrate materials is most manifested ; in order to prevent the metal being precipitated as its hydroxide, the higher form of the metal is made to combine in a complex while the lower form is incapable of giving a soluble complex, so that reduction of the reagent by the cellulose causes a coloured precipitate to be formed on the affected part of the fibre. The best known reagents of this type are Fehling's solution, copper sulphate made alkaline with caustic soda and the complex formed with sodium potassium tartrate ; and Braidy's solution, containing copper sulphate, sodium carbonate, and sodium bicarbonate to form the complex. In other copper reagents, complex formation depends on soluble citrates. In all these reagents the reducing action of the cellulose causes the deposition of a proportionate quantity of cuprous hydroxide. Other reagents are: Harrison's[1] reagent, which is an alkaline solution of silver thiosulphate—reduced to a brown precipitate, presumably silver sulphide ; Ditz's[2] solution, which is a Nessler reagent containing potassium mercuric iodide and caustic soda—reduced to a grey deposit which is probably metallic mercury; ferric ferricyanide (Ermen[3]) reduced to Prussian Blue. Other tests depend on the reduction of sodium hypoiodite (Bergemann and Machemer[4]), and upon the reduction of potassium permanganate (Kauffmann[5]) or of potassium ferricyanide (Freiberger[6]) by the alkaline extract of the affected cellulose. The two latter tests are not strictly comparable as they rely, not on mild oxidation of —CHO groups but on more thorough oxidation of carbohydrate material in an alkaline extract of cellulose. Thus they measure more nearly the alkaline dispersibility and hence the chain-length of part of the cellulose. It will be seen that the reducing properties of the degraded cellulose are thus measured or demonstrated by the action upon them of an oxidizing agent. The choice of this reagent and the exact conditions under which it is applied are important, since if the oxidizing action is too vigorous, the reagent attacks not only the degraded cellulose but also the unchanged cellulose, thus giving results which have a high and often erratic blank value and a low discriminating power for celluloses at different degrees of oxidation. For this reason methods based on the use of Fehling's solution are not greatly favoured, since the copper salt in the presence of caustic alkali is too active. All the reagents mentioned above have their uses, but probably most requirements may be met by the use of Harrison's reagent as a qualitative test and of the Braidy method as elaborated by the Shirley Institute[7] and

[1] Harrison, *J. Soc. Dyers and Col.*, 1912, **28**, 359.
[2] Ditz, *J. prakt. Chem.*, 1908, **78**, 343 ; Rhodes, *J. Text. Inst.*, 1929, **20**, T 55.
[3] Ermen, *J. Soc. Dyers and Col.*, 1928, **44**, 303 ; 1935, **51**, 127.
[4] Bergemann and Machemer, *Ber.*, 1930, **63**, 2304.
[5] Kauffmann, *J. Soc. Dyers and Col.*, 1924, **40**, 128.
[6] Freiberger, *J. Soc. Dyers and Col.*, 1930, **46**, 111.
[7] Clibbens and Geake, *J. Text. Inst.*, 1924, **15**, T 27.

by T. F. Heyes[1] for the determination of the copper number as a quantitative estimation.

Harrison's Reagent. Three solutions are required :—(*a*) 1 per cent. silver nitrate, (*b*) 4 per cent. sodium thiosulphate, (*c*) 4 per cent. caustic soda. Before use, equal volumes of the three solutions are mixed together, adding solution (*a*) to solution (*b*) (never in the reverse order) and finally solution (*c*).

The mixed solutions are heated to the boil and the sample immersed until the affected cellulose is stained and unoxidized cellulose is just beginning to show the formation of a pinky-brown colour. The sample is removed, rinsed in a fresh portion of solution (*b*) and finally washed with water. This test has been recommended for distinguishing between viscose and cuprammonium rayon, the samples of the rayon being boiled in the reagent for exactly one minute. The viscose stains a full deep brown, the cuprammonium a light brown. The test is not always to be depended upon for this purpose.

The Copper Number. This determination is greatly used in this country, and the procedure worked out by the Shirley Institute is almost universally employed. There are two versions, a normal-scale method using 2·5 g. of the sample and a micro method which represents the scaling-down by T. F. Heyes of the Shirley Institute procedure to use samples of 0·25 g. The former method is perhaps to be preferred when the estimation is carried out as a routine test for quality, so that large samples of the material are normally available, while the micro method is particularly adapted to the investigation of faults where the sample available may be small, or where small portions have to be examined for localized degradation. Since, however, the micro method is sufficiently accurate for almost every purpose, is not difficult to carry out, is quicker and does not involve the use of very large water-baths such as are necessary if many large-scale estimations are to be made at one time, it is recommended that the micro method be accepted as the standard method. When applied to the assay of large quantities of material it is more necessary to see that the sampling is thorough and efficient than when the large-scale method is employed. The following is the Heyes' micro method, modified in one or two details to increase the simplicity and the speed of the operation.

The following solutions are required :—

(*a*) Copper sulphate, $CuSO_4 . 5H_2O$ . . . . 100 g.
Distilled water to 1 litre.

(*b*) Sodium bicarbonate . . . . 50 g.
Sodium carbonate, cryst. . . . . . . 350 g.

(Half this amount of soda ash may be used, but since the solution is nearly saturated with respect to the carbonate, the crystalline salt is easier to bring

[1] Heyes, *J. Soc. Chem. Ind.*, 1928, 47, 90 T.

fully into solution. The sodium carbonate can be dissolved in hot water, but the solution should be cool before the bicarbonate is added.)

Water to 1 litre.

(c) Iron alum	100 g.
Conc. sulphuric acid	140 ml.

Water to 1 litre.

In preparing this solution, the iron alum crystals should be picked out by hand, those which have brownish patches or powdery efflorescence being rejected. The solution should be made up by diluting the sulphuric acid with most of the water and then adding the alum. The alum should not come into contact with the concentrated acid, since then the salt is dehydrated, and is difficult to dissolve.

(*d*) Dilute potassium permanganate solution which should be standardized before use and adjusted to $0{\cdot}924 \times N/25$ exactly.
(*e*) $2N$ sodium carbonate solution tinted for identification purposes with a trace of phenolphthalein.
(*f*) $2N$ sulphuric acid.

The apparatus required is as follows :—

Test-tubes of Pyrex or Monax glass, rimmed, 15-17 ml. capacity, with pear-shaped hollow glass bulbs to act as stoppers and air condensers for the tubes.

A cylindrical water-bath somewhat deeper than the length of the test-tubes, fitted with constant level arrangement and tight-fitting lid. The lid should be bored with holes to take the test-tubes, but slightly smaller in diameter than the rims of the tubes.

A micro-burette, 5 ml. total capacity, graduated in 0·01 ml. The burette should have a three-way cock so that it may be filled from below by a reservoir connected by glass tubing with the side arm of the stopcock. It is difficult to fill a micro-burette from the top. The barrel of the stopcock should be as large as possible and should be ground in with great care so that it works with smoothness and requires the minimum of lubricant. The jet of the burette should taper somewhat and should be at least 2 ins. long. It is not advisable to have a very fine bore.

A filtration apparatus made from a conical funnel with sintered glass plate, Jena 39 G 3, the receiver being a tall-form 100 ml. beaker. The receiver should be made from as white a glass as possible, and the greenish or yellowish resistance glasses should be avoided.

Two thin glass stirring rods of distinctive shapes.

If the titrations are to be performed by artificial light, it is necessary to illuminate the working bench with the light from two " daylight " lamps, fitted with reflectors and suspended at least 5 ft. above the bench surface. A batch of titrations should never be carried out partly by daylight and partly by artificial light.

The material to be tested, if in the form of yarn, is cut into short lengths (2 to 3 mm.) and the cuttings are well mixed. If the material is in the form of cloth, it is cut into strips about 2 mm. broad. The strips are cut diagonally across the warp and weft so that both sets of yarn are disintegrated.

In weighing out a sample for one determination, 0·25 g. of the air-dry cotton should be taken, so that an allowance for the moisture

content should be made. It is not usually necessary to determine the moisture content, an average value for the type of material and the conditions of the laboratory usually giving results of sufficient accuracy, but if a moisture determination is made upon the material under examination by heating it to constant weight, the portion that has been used for the moisture determination should not be used for determination of the copper number.

The water-bath is heated to boiling, a mixture of solutions (*a*) and (*b*) in the proportion of 5 ml. of (*a*) to 95 ml. of (*b*) is brought almost to the boil, and 10 ml. of the mixture placed in each test-tube. Into each tube a weighed portion of the cotton is introduced, and the tube stoppered with a bulb and placed immediately in the water-bath. During the first fifteen minutes each of the tubes in the bath should be examined frequently and if the cotton rises to the top, the reagent solution should be stirred with a thin glass rod or piece of copper wire. This precaution is very important since, if some of the cotton comes into contact with the air while saturated with the hot alkaline reagent, further oxidation of unchanged cellulose may result, giving a fictitiously high copper number. The water in the water-bath should be kept at a vigorous boil during the whole time of the experiment, and the bath should be protected from draughts so that the water does not become cooled on occasion below its boiling point. The water of the bath should be kept at a constant level, and above the level of the copper reagent in the test-tubes when these are fixed in the bath in their normal position ; otherwise a ring of black cupric oxide may be formed on the walls of the tube just above the reagent solution.

The boiling should continue for exactly three hours. The tubes are then removed and placed in a stand to cool. The estimation of the liberated cuprous oxide should not be delayed for more than two or three hours.

In carrying out the estimation, the micro-burette should first be washed out and then filled with the $0{\cdot}924 \times N/25$ permanganate solution. A portion of solution (*c*), sufficient for the full series of determinations to be made, is first taken and any small quantity of reducing matter that may be present is destroyed by adding the permanganate solution until a very faint pink colour is obtained. Some more of the untreated solution (*c*) is then added until the pink colour disappears. In this way, an iron-alum solution of a very low blank value is obtained.

The filtration apparatus should now be connected to the pump, having first made sure that both filter and receiver are washed clean and free from acid picked up during a previous determination. The contents of the tube are filtered through the sintered plate, and the

filtrate is rejected. 5 ml. of the $2N$ carbonate solution is then placed in the tube, stirred round, poured over the cotton on the filter and sucked through. This solution is also rejected. The tube is then washed out with 10 ml. of hot water, the washings poured over the cotton, and then slowly drawn through the filter. These washings are also rejected.

The filtration apparatus is now disconnected from the pump, and 5 ml. of the iron alum solution is poured into the test-tube, stirred round (a separate stirring rod is reserved for this and the succeeding stages, and should not be used in the stages previous to alum treatment) and then poured over the cotton on the filter plate. This solution should remain in contact with the cotton for two minutes and should then be sucked through into the receiver. Where heavy deposits of cuprous oxide are present on the cotton, the red colour will turn to a grey before disappearing, and the alum solution should then remain in contact with the cotton for at least two minutes after the grey colour has disappeared. This process is repeated with a further 5 ml. of the alum solution and finally with 5 ml. of the $2N$ sulphuric acid solution. If the alum solution has been corrected with permanganate as described above, there will be no necessity to measure it out with great accuracy in the operations just described, and the time of the operation is thereby shortened.

The combined acid filtrates are then titrated with the permanganate solution. To prevent drop formation on the jet of the burette, a serious matter in micro-titrations, the jet should first be touched with a filter paper and then inserted with its end a few millimetres below the surface of the liquid to be titrated. The permanganate solution is added a little at a time—a smooth-acting stop-cock is of value—until the green colour of the solution suddenly appears to turn much whiter. The burette should then be read, and if the addition of a further 0·01 ml. of permanganate causes the solution to turn a faint but definite pink, the reading should be accepted as corresponding to the true end-point A blank experiment is performed on a mixture of 10 ml. of the alum solution and 5 ml. of the sulphuric acid, and the permanganate value of the blank should be subtracted from the value for the cotton.

The copper number is defined as the weight of copper in grams which is changed from the cupric to the cuprous state by 100 g. of bone-dry cotton. It will be found that the copper number is given directly by the net number of cubic centimetres of permanganate used if the solution is exactly $0{\cdot}924 \times N/25$. It is difficult to give values for the copper number which are fully representative of the different classes of modified cellulose owing to the influence of a number of conditions other than the oxygen consumption on the copper number

of oxidized cellulose, and to the fact that celluloses with reducing properties are produced both by the action of acids and of oxidizing agents. However, the following figures will act as a rough guide.

Material.	Copper number.
Grey cotton yarn	Between 1 and 2 according to origin and thoroughness of blowroom, carding, and combing processes
Water-boiled grey cotton . .	About 0·3
Laboratory scoured yarn . .	0·005-0·01
,, bleached yarn . .	0·05-0·1
Good commercial bleach . .	Up to 0·1
Satisfactory commercial bleach .	Up to 0·2
Slight overbleaching . . .	Above 0·2-0·4
Moderate overbleaching . .	0·4-0·9
Severe overbleaching . . .	Above 0·9

The following figures are given by Ridge, Parsons and Corner[1] for the copper numbers of many varieties of Rayon examined by them :

Rayon.	Copper number.
Viscoses (17 types)	0·8-1·5
Staple fibre (2 types)	0·9
Lilienfeld rayons (3 types)	0·8-1·5
Cuprammonium rayons (7 types)	0·5-1·5
Nitrocellulose (1 type)	2·7 *
Cellulose acetate rayons (4 types)	3·0 *
Esterified cotton (2 types)	1·0-1·2
Bleached cotton linters	Below 0·5

* It is doubtful whether the copper number has any significance as a measure of the degree of degradation of the cellulose for these rayons.

Celluloses degraded by acid action as well as those tendered by oxidizing agents possess higher reducing powers than the normal cellulose if they have not subsequently been subjected to the action of alkalis. The copper number alone is therefore not capable of distinguishing between damage caused by acids and that caused by oxidizing agents. Since certain of the common mineral acids and also some of the organic acids, especially oxalic, are often retained by the cellulose with great tenacity, it is sometimes possible to distinguish acid tendering by showing the presence of appreciable quantities of acid in the fibre, when the tendering has occurred by the drying-in of the acid during processing. Where tendering has occurred by prolonged treatment with warm dilute acid solutions, this test is not so reliable, and it is safer to attempt a diagnosis by comparing the value

[1] Ridge, Parsons and Corner, *J. Text. Inst.*, 1931, **22**, 117 T.

for the copper number with the values for the strength, fluidity and other constants of the degraded cellulose. This will be dealt with later, but it should be mentioned here that present-day work on the degradation of cellulose gives very strong support to the view that one of the most important distinctions between acid and oxidative tendering is that the former gives rise to products with an enhanced reducing power only, while the latter gives rise to modified celluloses which may have a more or less enhanced reducing power, but which also have properties corresponding to the formation of carboxyl groups during the degradation. The detection and estimation of the magnitude of carboxyl formation has been proposed by a number of different methods. For instance, the methylene blue estimation, put on a quantitative basis by Clibbens and other workers,[1] when the maximum absorption of dye takes place from neutral solutions, seems to be connected closely with the carboxyl formation. So does the alkalinity of the ash determined by the method suggested by the same authors.[2] The higher absorption of basic stannous chloride by oxidized as compared with acid-degraded celluloses, observed by Haller [3] is probably to be referred to the same distinction between the two types of product. The methylene blue absorption is not a very easy determination to carry out without a good deal of practice and it requires to be carried out both from an acid solution and from a neutral solution to enable a certain distinction to be made. The ash alkalinity also requires some practice before it can be carried out with full success, and it is liable to be interfered with by a number of irrelevant factors. It is to be therefore recommended that a direct determination of the carboxyl content of the cellulose under examination be made. Observations and deductions by Schwalbe [4] and by Neale [5] have shown how this may be done successfully. According to Neale, the direct titration with alkali of the carboxyl groups in oxidized cellulose is not possible since the anion of the carboxylic acid is part of the cellulose structure and is therefore immobile. This restricts the normal freedom of ionization found in soluble acids. If, however, the oxidized cellulose is first treated with a strong solution of an electrolyte, such as common salt, an interchange takes place between the hydrogen of the carboxyl group and the cation of the electrolyte. The hydrogen is then combined in a strong acid, and its estimation by alkali is possible.

Carboxyl Group Determination. The carboxyl groups in the

[1] Clibbens and Geake, *J. Text. Inst.*, 1926, **17**, 127 T.

[2] Birtwell, Clibbens and Ridge, *ibid.*, 1923, **14**, 297 T.; *cf.* Fargher and Probert, *ibid.*, 1926, **17**, 46 T.

[3] Haller, *Textilber.*, 1931, **12**, 257.

[4] Schwalbe and Becker, *Ber.*, 1921, **54**, 545.

[5] Neale and Stringfellow, *Trans. Faraday Soc.*, 1937, **33**, 881.

modified cellulose may be present in the form of their sodium salts. It is necessary therefore to treat first with dilute acid to liberate the carboxyl groups.

A weight of cotton corresponding to 1 g. of the bone-dry material is cut into small pieces and treated at room temperature with $2N$ hydrochloric acid solution for one hour. It is then washed with a number of changes of distilled water until the washings are neutral to brom-cresol purple. After this it is washed twice with distilled water free from carbon dioxide. 20 ml. of a 5 per cent. solution of pure sodium chloride made up with carbon dioxide-free water, 6 drops of B.D.H. brom-cresol purple solution and 20 ml. of $N/50$ caustic soda solution, accurately standardized, are added. During the addition of these solutions a current of air which has been freed from carbon dioxide should be passed into the flask. This current should be maintained for ten minutes longer and then the flask should be securely stoppered and set aside for one hour. The standard caustic soda solution should be made from carbonate-free reagent, using carbon dioxide-free water. It should be stored in a bottle of Jena high-resistance glass, under an atmosphere of carbon dioxide-free air, and should pass therefrom into a burette also of chemically resistant glass, such as Pyrex. The titration flask is conveniently made from Pyrex or similar glass and provided with a ground-in stopper. During standing the flask should be shaken gently from time to time. At the end of the hour the excess caustic soda should be titrated with standard $N/50$ hydrochloric acid, a current of carbon dioxide-free air being passed into the flask during the titration. The titration is carried to the neutral colour of brom-cresol purple (range pH 5·2 to 6·8). From the amount of caustic soda used, the number of carboxyl groups is calculated, the result being usually expressed in milli-equivalents of COOH per 100 g. of bone-dry cellulose. The carboxyl content of a carefully bleached cotton cellulose is of the order of 0·5 milli-equivalents per 100 g. The figure for a cellulose degraded solely by the action of acids is not very much greater. The values for celluloses attacked by oxidizing agents range from about 0·8 for incipient attack to about 5 for severe attack where the cotton is beginning to disintegrate. For a given uptake of oxygen, the value is greater when the attack has been carried out under alkaline conditions than when it has been carried out under acid conditions.

The Determination of Cuprammonium Fluidity

The analytical methods described above depend for detecting the fact of modification or for estimating its severity upon the detection or estimation of modification products of cellulose having

properties distinguishing them from the parent substance. These methods work well when the conditions of modification are such as to produce well-defined degradation products which remain on the fibre, but fail when subsequent treatments undergone by the material cause a further modification or a removal of the modification products. At the same time, while removing the chemical evidence of the damage, these later treatments cannot restore the cellulose to its former condition, repairing the damage that has occurred, so that it is often found that evidences of damage furnished by the chemical tests do not correspond to the evidences of damage furnished by, for instance, the low tensile strength of the material. As mentioned at the beginning of this section, low tensile strength does not necessarily arise from chemical modification of the cellulose, but may come from causes purely mechanical, so that it is important to find a method which can detect and assess chemical damage, and which does not depend upon the reactional properties of the modified material. Such a process is furnished by the measurements of the viscosities of cellulosic materials dissolved at standard concentration in a solution of cuprammonium hydroxide of specified composition. The farther the cellulose under test has departed from its native constitution the lower will be the viscosity. The work of Staudinger has shown that there is a close relationship between the length of the chain-molecules of such a polymerized substance as cellulose and the viscosity of its solutions, and it is known that practically any chemical change undergone by cellulose results in a shortening, actual or potential, of the average length of its molecules. Therefore the diminution in the cuprammonium viscosity, or a rise in the reciprocal value of cuprammonium fluidity, may be accepted as certain evidence of chemical breakdown or depolymerization. Only when the degree of comminution is very great indeed do mechanical influences affect the fluidity. The preparation of standard solutions of cellulose in cuprammonium hydroxide solution and the subsequent measurement of their viscosity, was formerly somewhat complicated and troublesome owing to the necessity for the complete exclusion of air during the two processes. Cellulose dissolved in the alkaline solvent is very sensitive to atmospheric oxidation and then suffers further lowering of the viscosity. The reagent is also oxidized by the air and is thereby rendered less suitable for use. For cotton and viscose materials, the method elaborated by Clibbens and Geake [1] at the Shirley Institute overcomes these difficulties in a very satisfactory manner.

The cuprammonium solution (for the preparation of which the original paper should be consulted) should contain 240 g. of ammonia

[1] Clibbens and Geake, *J. Text. Inst.*, 1928, **19**, T 77; *cf.* Clibbens and Little, *ibid.*, 1936, **27** T.

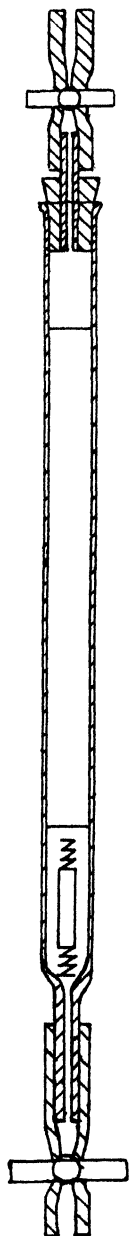
(as NH_3) and 15 g. of copper per litre. It should be free from other inorganic electrolytes and the nitrite content should not exceed 0·5 g. of nitrous acid per litre.

The same vessel serves for dissolving the cellulose and for measuring the viscosity. A sketch is given in Fig. 130. The barrel of the viscometer is 26 cm. long and has an internal diameter of 1 cm. The capillary is 2·5 cm. long, 0·88 mm. in internal bore and 6 mm. in external diameter. Two rings are etched on the barrel at heights of 6·2 and 24·2 cm. vertically above the flat end of the capillary. Another ring is etched about 0·7 cm. below the mouth of the barrel to serve as a guide for the insertion of the upper stopper so that the viscometer shall enclose approximately the same volume each time that it is filled. The capillary is closed by slipping over it a short length of pressure tubing closed at the lower end with a screw clip. The mouth of the barrel is closed by a rubber stopper through which passes a short length of capillary tube. At the lower end of the stopper, the capillary tube is flush with the rubber, but on the outer end it projects for a short distance. On this projecting end is a short length of pressure tubing also closed with a screw clip. As a stirrer a length of ¼ in. steel rod, 1 in. long, with short lengths of spiral spring of approximately the same diameter soldered at either end, is placed in the barrel. The end of each of these springs should be turned inward so that when the viscometer is held horizontally and the stirrer is resting at the bottom, the end of the capillary is not blocked. The original chisel-shaped stirrer described by the Shirley Institute is not to be recommended since after a period of use a circle of chipped glass at the lower end of the viscometer is formed, and the capillary often breaks away while the viscometer is in use. The mercury also recommended as a stirrer has the disadvantage that it occasionally forms a very stable emulsion in the cuprammonium solution. If mercury is used, 0·7 ml. is run in from a burette each time a solution of cotton is prepared in the viscometer. It is a good plan to cover the mercury in the burette with a few ml. of a dilute solution of mercurous chloride, and to read the meniscus of this liquid rather than the less familiarly shaped meniscus of the mercury. The effective volume of the viscometer is obtained by inserting the stirrer, suspending the viscometer

Fig. 130.

vertically, covering the end of the capillary with the finger and running in distilled water from a burette until it reaches the ring etched near the mouth of the barrel. This method is to be preferred to the usual method of weighing the viscometer first empty and then filled with distilled water, since it is doubtful if the cuprammonium held in the rubber tubing and in the upper capillary can play much part in dissolving the cotton.

The viscometer is calibrated by filling it to the mouth with a glycerine-water mixture of known viscosity and allowing the liquid to flow freely through the capillary while the viscometer is suspended vertically. The time required for the liquid to pass between the lower pair of etched rings is noted. The experiment should be carried out at a fixed temperature of 20°. A constant for the viscometer is obtained thus :

$$C = \frac{\text{density} \times \text{time}}{\text{viscosity}} \text{ or } C = \text{density} \times \text{time} \times \text{fluidity}.$$

It is convenient to use as the standard liquid a mixture of glycerine and water (approximately 64·4 per cent. by weight of glycerine) which has been adjusted to a sp. gr. of 1·1681 in air at 20°, compared with water at 20°. The fluidity of this liquid is 6·83 c.g.s. units at 20°. For glycerine-water mixtures at other concentrations, a table connecting the sp. gr. with the viscosity is given in Archbutt and Deeley's *Lubricants and Lubrication*, 5th and later editions.

To prepare the cuprammonium solution of the material under examination, the cloth or yarn is cut into small pieces as for the copper number determination and the chopped material is well mixed. The quantity necessary to produce a concentration of 0·5 g. of bone-dry cotton per 100 ml. of solution in the volume of liquid held by the viscometer is weighed into a short length of glass tube, about ½ cm. bore and 2 in. long. The lower rubber tube and clip is placed in position on the end of the capillary, and the viscometer is two-thirds filled with cuprammonium solution. The screw clip is opened to allow a few drops of the solution to pass through and to fill the capillary. It is then screwed up. The weighed cotton in the glass tube is then pushed by means of a glass rod into the cuprammonium solution, care being taken that as little as possible of the cotton sticks to the uncovered walls of the viscometer. A little more of the solution is rinsed round the walls of the barrel, the stirrer is inserted, the viscometer is tapped to free any air bubbles that may have been carried in with the cotton, and the viscometer is then filled to the brim with the solution. The clip on the upper stopper is opened and this stopper is inserted and pushed down until its lower surface is on a level with the etched ring just below the mouth. Care should be

taken that no air is entrapped in the viscometer during this operation and that the excess solution flows out through the upper capillary and its attached rubber tube as in a specific gravity bottle. The upper clip is then screwed up and the viscometer is ready for the stirring operation. Care should be taken that the screw clips are screwed up sufficiently to prevent any possibility of the solution escaping or of air entering, but not so tightly that they cut into the rubber, otherwise leaks will develop while the solution is being stirred.

Stirring must be carried out in the absence of light. A convenient apparatus for this operation consists of a shallow rectangular box. One of the large sides of the box is a hinged lid. The opposite corresponding side is fitted with small clips in pairs to hold the viscometers. The box is fitted with trunnions so disposed that it can rotate and turn the viscometers end over end. The box is moved by a small electric motor working through a worm reduction gear so that the viscometers are turned end over end about four times in a minute.

Most celluloses are completely dissolved if the stirring is carried out overnight, but if grey material is being examined, it is wiser to allow longer, since the experiment is vitiated if complete solution is not achieved, and it is somewhat difficult to tell by inspection when this stage is reached.

The viscosity of the solution depends upon the temperature, and for accurate work it is customary to run out the cuprammonium solution while the viscometer is suspended in a special glass sleeve which is in turn suspended in a glass-fronted thermostat maintained at 20°. For many purposes it is sufficient to place the viscometers in a bath of water, kept at the correct temperature for half an hour before the measurement is to be made. The viscometers are removed as they are required, wiped well, held vertically in a burette stand, placed out of the way of draughts, and the time of outflow of the cotton solution measured with stopper and rubber tubing removed from the viscometer. The fluidity of the solution is expressed by the formula

$$F = \frac{C}{0{\cdot}93 \times \text{time of outflow}}.$$

0·93 is here the assumed density of the cuprammonium solution. To avoid using this value in each calculation, a new constant $C' = C/0{\cdot}93$ is calculated for each viscometer, and the fluidity is then given by $F = C'/T$. This simple expression is adequate for most technical purposes. For cottons with high fluidity, the rate of outflow through the viscometer capillary is high, and the liquid leaves with an appreciable velocity and possesses therefore considerable kinetic energy ; thus all

the potential energy stored in the head of liquid above the capillary is not utilized in overcoming the resistance to flow of the liquid through the fine bore. The time of flow is therefore increased, and the fluidity appears less than it should be for the degree of degradation of the cellulose. This deviation becomes appreciable for fluidities higher than 30, and for more correct expression of the fluidity, it may be calculated from the following equation :

$$dF = C/(T-K/T)$$

where d = the density of the solution, T = time of outflow, C = the constant of the viscometer and has the same significance as in the previous equations, and K is another constant for the instrument.

$$K = C\times(1\cdot 12\ V/8\pi l)$$

where V = the volume between the two timing rings and l = the length of the capillary.

Most of the regenerated cellulose products such as rayons and viscose foils have very high fluidities as compared with native cellulose products, and the discrimination to be obtained in the fluidities at the standard concentration of ½ per cent. for materials at different stages of degradation is not very high. The Shirley Institute therefore recommend that these materials be made into a solution of 2 g. per 100 ml., and the fluidity determined at this standard concentration. If this is done the relations between the change in fluidity and the percentage decrease in strength on further modification of the cellulose are approximately the same for each class of material. The following table will give some idea of the fluidities of typical materials.

	Fluidity (0·5 per cent. solution).	Fluidity (2 per cent. solution).
Grey cotton yarn	Less than 1	...
Careful lab. scour	Up to 2	...
,, pressure boil	,, 3	...
Best commercial bleaching	4	...
Upper limit for satisfactory commercial bleach	10	...
Distinct degradation	20	...
Severe degradation	30	...
*Viscoses (17 types)	...	8 to 14
*Staple fibre (2 types)	...	4 ,, 10
*Lilienfeld (3 types)	...	3 ,, 6
*Cuprammonium (7 types)	...	3 ,, 7
Nitrocellulose	...	17
*Cellulose acetate (4 types)	...	53 to 54
Esterified cotton (2 types)	...	4 ,, 6
Cotton linters (bleached)	...	1 ,, 4

* Since the publication of these results in 1931, there has been a distinct and steady increase in the quality of the cellulose in most of the best-known brands of cellulosic artificial fibre.

The determination of the fluidity of the bast fibres has been carried out by workers at the Linen Research Association's laboratories,[1] and it has been found that purified linen cellulose always contains a small proportion of material insoluble in cuprammonium solution. They have therefore designed an apparatus in which the solution is filtered out of contact with air before it is placed in the viscometer. For details of this apparatus, the original paper should be consulted.

Clibbens and Little [2] have recently described a micro-viscometer in which the approximate fluidity of a material may be determined when only a few milligrams are available. In the same paper is given some supplementary information about the determination of fluidity by the standard method.

Many materials, like the regenerated cellulose fibres, which have a high fluidity dissolve very quickly, and it is possible to make the solutions of the cellulose in stoppered bottles, making sure that the greater part of the bottle is filled with liquid, and shaking the bottle for one or two hours. In this time the influence of oxygen on the dissolved material is scarcely perceptible. Enough solution for several determinations may thus be prepared much more quickly than by the normal method described above.

The most satisfactory method of preparing cuprammonium hydroxide solution is that of Clibbens and Geake, described in *The Methods of Cellulose Chemistry*, by C. Dorée. Bright copper powder may not be sufficiently active but precipitated copper [3] or very finely divided cuprous oxide work well.

Interpretation of the Results of Cellulose Analysis

A summary can now be given of the interpretation of relations of the tensile strength, fluidity, copper number, and carboxyl value of a given cellulosic material. It must again be emphasized that the properties of oxidized celluloses differ in important respects according as they are formed by the action of reagents acting in an acid, neutral, or alkaline medium. One property of oxidized celluloses produced by acid oxidizing solutions is often of great value for diagnostic purposes : the full fall in tensile strength and rise in cuprammonium viscosity, corresponding to the consumption of oxygen, is not manifested immediately after the action by the reagent. On boiling with alkaline solutions, however, a further fall takes place in the tensile strength, as well as a rise in the fluidity, until the normal value, corresponding to the same intensity of attack in alkaline solutions of the oxidizing agent, is reached. Modified celluloses produced by the action of

[1] Kinkead, *J. Text. Inst.*, 1931, **22**, 411 T. [2] *Loc. cit.*

[3] Made by Messrs Burgoyne, Burbidges and Co., East Ham, London.

acids or of alkaline solutions of oxidizing agents show only a relatively slight decrease in strength and increase in fluidity on alkali boiling unless the degree of modification is very high, but under all circumstances this change, on alkali boiling, in the properties mentioned is much less than the change which takes place in celluloses modified severely with acid or neutral solutions of an oxidizing agent. The relationships between the different properties may therefore be summarized as in the accompanying table :—

Type of attack.	Tensile strength before alkali boil.	Tensile strength after alkali boil.	Fluidity before | after alkali boil.	Copper number.	Carboxyl content.
Acid	Proportionate to severity of attack	Not greatly altered by boil	As for tensile strength	Proportional to severity of attack	Low, scarcely greater than good cotton
Alkaline oxidation	,, ,,	Small alteration	,, ,,	Low, relative to severity of attack	High, relative to severity of attack
Acid oxidation	Low, relative to severity of attack	Greatly altered by boil	,, ,,	High, relative to severity of attack	Low, relative to severity of attack

Approximately parallel to one or the other of these main properties are others which can be grouped as follows :—

Parallel to Copper Number. Solubility in hot dilute alkalies is generally greater in the reducing type of cellulose for a given intensity of attack. The tendency of the modified cellulose to yellow on heating, storage, or treatment with dilute alkaline and detergent solutions, is greater with the reducing type of modified cellulose.

Parallel to Carboxyl Value. The absorptive power of the modified cellulose for methylene blue (from neutral solutions), and various metallic ions, the ash alkalinity, and to the decrease in the absorption of direct dyes.

Tests for the Identification of Mercerization and for the Assessment of the Completeness of Mercerization

Probably the simplest and most certain tests for the distinction of mercerized from unmercerized cotton depend on the change which takes place in the external appearance of the fibre during the mercerization process. Depending on the thoroughness of the treatment, a greater or less proportion of the hairs in a given cotton textile structure are changed, and the normal shape, resembling a rather thick twisted ribbon, is altered until practically all the convolutions

disappear, and the hair becomes rod-like in form. The efficiency of the mercerization treatment may be measured by the number of hairs in which the convolutions have disappeared completely, expressed as a percentage of the total number of hairs examined. There are some hairs in a given sample of cotton which respond very rapidly to mercerization treatment, while others show a greater resistance to change, and hairs with a whole range of resistances up to the completely unmercerizable are found. Therefore the percentage of fully mercerized hairs in a given sample is a useful indication of the completeness of contact between the mercerizing alkali and the cotton during the technical process, of the duration of contact, and of the suitability of the alkali solutions used with respect to concentration, temperature, and other factors which influence the final result. Moreover, under specified conditions, the mercerization percentage as it is called is an indication of the amount of a substantive dye which will be taken up by the mercerized material. Although it is not strictly a chemical method, a simple method of making the mercerization count under the microscope may conveniently be described here[1] (see also p. 655).

Two safety-razor blades are clamped side by side with their edges parallel to each other. Owing to the rake, the actual edges are a short distance apart, corresponding to about the distance occupied by two convolutions in the cotton hair. The cotton to be examined, in the form of yarn, is wound round a piece of soft wooden rod over 2 in. in circumference. Several turns of yarn are wound one on the top of another, so that a compact band about as deep as it is broad encircles the wood. This band is then cut across by the clamped blades. The mass of cut hairs between the blades is brought out by means of a needle and placed in the centre of a microscope slide. A drop (not too large) of medicinal paraffin is placed on the top of the cut hairs, and these are mixed very thoroughly into the paraffin with the point of a needle, care being taken that the area of the drop is not spread unduly during the mixing. Mixing should be continued until examination under the microscope shows that all the small portions of cotton hair are separated and evenly distributed through the mounting fluid. A cover-glass is then placed in position and the slide examined under a microscope, preferably with a mechanical stage. The area under the cover-glass is systematically traversed in strips rather wider than the field of the microscope, and a simultaneous count is made of the total number of hairs and of the number of hairs in which no sign of a convolution remains. The latter total expressed as a percentage of the total number of hairs examined is the simple mercerization percentage and will be sufficient for most purposes.

[1] Calvert and Clibbens, *J. Text. Inst.*, 1933, **24**, 233 T.

In this examination, the amount of cotton taken on a single slide should not be so great that the fragments are unduly crowded together. Since a reasonable depth of focus saves refocussing frequently as one hair after another is examined, a $\frac{2}{3}$ in. objective should be used, but in order to avoid having too many fragments in the field at once the highest available magnification should be used at the eye-piece. For one cotton sample, a count of 200 to 400 fragments is usually adequate to determine the mercerization percentage.

Besides a direct test such as the one described above, there are a number of chemical tests designed either to distinguish mercerized from unmercerized cotton or to determine the degree of mercerization. Fundamentally, practically all of them depend on the fact that mercerized cotton has a greater absorptive power and a higher reactivity than unmercerized. Most of these tests are better adapted for qualitative than for quantitative purposes.

A number of tests depend on the fact that if mercerized cotton is treated with a solution which contains a fair concentration of iodine along with a substance that possesses some ability to swell or to disperse cellulose, a blue coloration similar to the starch-iodine colour results. Normal cotton does not give this coloration. Hübner, for instance, prepares such a reagent by mixing together a dilute iodine solution and a concentrated solution of zinc chloride. One of the simplest methods is that proposed by Ermen.

In this method the reagent is prepared by dissolving 6 g. of iodine in a strong solution of potassium iodide (50 g. in 50 ml. of water). The material to be tested is stripped if necessary from dyestuff, and immersed in a very dilute solution of iodine (pale yellow). If a blue coloration develops in less than five minutes, the material is boiled for a few minutes with $N/10$ hydrochloric acid and well washed in hot water, this treatment being repeated until no starch coloration is obtained with the dilute iodine. A small portion of the desized sample together with a small piece of mercerized cotton and a piece of unmercerized cotton are placed in a beaker and are covered with the reagent. After five minutes the iodine solution is poured back into its bottle and the pieces are washed a number of times with small quantities of water (if large volumes of water are used for washing, the potassium iodide is removed before the excess iodine, and the washing process is prolonged). Washing is continued until the unmercerized piece is almost white in colour while the mercerized piece is still a full blue. The state of the unknown sample can then be determined by comparison with these two standards. Results are mostly unambiguous, but occasionally a sample of cotton that has been heavily scoured but not mercerized will colour a faint blue and will cause some doubt. The blue colour with any of these iodine

reagents is not permanent, since the iodine is very loosely combined and escapes in time by sublimation or perhaps by oxidation of the cellulose. To preserve the colour it is suggested by Ermen that the cotton bearing the blue iodine compound be immersed at once, after washing, in a warm solution of Indigosol OR containing a trace of added acid. The iodine oxidizes the indigosol and develops a roughly equivalent quantity of vat dye on the material. The material must then be soaped thoroughly to remove excess of indigosol.

In the simpler methods of carrying out the iodine test it is difficult to know when the free iodine has been removed and when the washing process is also removing some of the iodine from the blue compound. For this reason it is difficult to base a quantitative test upon these operations alone, since the efficiency of the washing treatment, and hence of ultimate colour, is affected by such irrelevant factors as the local irregularities of twist and weave in the material. I. Schwertassek [1] has, however, worked out a method in which the washing is carried out by treatment of the cotton with saturated solutions of sodium sulphate under standard conditions. The amount of iodine remaining in the cloth after washing is estimated by titration.

Semi-quantitative and quantitative methods depending upon the enhanced reactivity and absorptive power of the cellulose have been suggested by various authors. For example :—

D. Clibbens and others.[2] Rise in copper number after standard oxidizing treatment with sodium hypobromite.

V. G. Abozin.[3] The material is saturated with a solution of sulphuric acid of known strength, heated at a fixed temperature for a fixed time and the copper number determined.

Mennell.[4] The material is immersed for five minutes in strong sulphuric acid containing formaldehyde. Presumably the sulphuric acid causes further increase in the internal surface in proportion to the original degree of mercerisation, for on washing and dyeing with Chlorazol Sky Blue GW the mercerised material dyes the more deeply. The formaldehyde prevents the too rapid swelling by the sulphuric acid, apparently by formation of methylene-ether links between the cellulose chain molecules.

Neale.[5] The absorption of barium hydroxide under standard conditions is dependent on the degree of mercerization.

If cotton has been fully mercerized, it will not acquire further affinity for direct dyestuffs if it is again treated with alkali at mercerizing strength. One test which makes use of this fact is carried out as follows :—

A solution of caustic soda of 76° Tw. is made and is also used to prepare two other solutions, one by dilution with an equal volume of water and one by dilution with twice the volume of water. The

[1] Schwertassek, *Textilber.*, 1931, **12**, 457. [2] *J. Text. Inst.*, 1930, **21**, 96 T.
[3] *Brit. Chem. Abstr. B*, 1935, 989. [4] Mennell, *J. Text. Inst.*, 1926, **17**, 247 T.
[5] Neale, *J. Text. Inst.*, 1931, **22**, 320 T, 349 T.

cloth to be tested is spotted with each of these solutions, washed, soured with dilute sulphuric acid, washed well and dyed in Congo red. If the cotton has already been mercerized the spotted places will not dye appreciably deeper than the rest.

VI. THE QUALITATIVE ANALYSIS OF COMMERCIAL DYESTUFFS

By EVA HIBBERT, M.Sc. (Tech.)

One of the best methods of identifying any dyestuff is to ascertain the relative dyeing affinity of the product for the various natural fibres and for artificial silks (especially acetate rayon). Following this, the dyed material may be tested by a system which comprises the reactions on the fibre, such as varying solubility (stripping action) in organic solvents and water, the action of reducing agents, oxidizing agents, acids, and alkalis. In certain cases variation in resistance to attack may be observed in compounds of rather similar constitution and compounds of similar constitution are known to appear in different dyeing groups. Thus, Azo-compounds are found in the direct cotton and wool dyeing groups, but Bismarck brown, a basic colour, is an azo-colour and Alizarine yellow A is also an azo-colour.

Dyestuffs Soluble in Water

Dyestuffs with definite solubility in water belong to five dyeing groups. The solubility may be only about 1 per cent. and is frequently lower, but a considerable appearance of colour is imparted to water and a spot on filter paper reveals the absence of undissolved particles. The soluble dyestuffs include :—

1. Direct cotton colours (Chlorazol, Chloramine, Chlorantine, Benzo).
2. Acid wool colours (Coomassie, Disulphine, Lissamine).
3. Basic colours (Acronol, Methylene blue, Methyl violet, Rhodamine).
4. Soluble colours for acetate rayon (Solacet).
5. Acid chrome colours—sulphonated mordant colours—(Solway).

The names bracketed represent examples of the types, and in many cases other names are commonly recognized by dyers (see Colour Index). If small quantities of cotton, wool, and acetate silk are placed in the aqueous solutions and if in groups 1, 2, and 3, a further test is made in the presence of a drop of acetic acid, definite deductions may be made from the appearance of the dyed fibres. Cotton is dyed better in the direct colours without acetic acid, but wool is dyed better when acetic acid is present. Cotton is not dyed in acid colours with or without

acid, but wool is dyed deeply in the presence of acid. Cotton is only stained slightly in basic colours, whilst wool is dyed deeply both with and without acetic acid, but usually dyes best without acid if the same quantity of colour is used for each dyeing. Acetate rayon is dyed in basic colours, but in most cases a basic colour dyed on rayon appears different in tone from the same colour dyed on wool. Cotton is not dyed in acetate rayon colours, wool is dyed best from an acid bath and better shades are obtained by dyeing acetate rayon in the ordinary aqueous solution. As the name indicates, these colours are specially adapted for dyeing acetate rayon. Acid mordant colours may be detected by the fact that they only give a really satisfactory shade on chrome mordanted wool. The chrome mordanted wool is obtained by boiling wool with potassium dichromate solution and a little cream of tartar. As a further dyeing test for a basic colour its superior dyeing of cotton treated with tannic acid and fixed in tartar emetic as compared with the dyeing on untreated cotton is noteworthy. Additions of sodium chloride and sulphate cause darker shades to be obtained with direct colours on cotton. Sodium sulphate slows down the dyeing of wool from an acid bath, but does not prevent the fibre from taking up the colour completely.

The outstanding effects are tabulated below :—

No.	Dyestuff group.	Cotton.	Tanned cotton.	Wool.	Wool and acetic acid.	Wool, chromed.	Acetate rayon.
1	Direct cotton . .	Dyed	...	...	Dyed	...	...
2	Acid (wool) . .	...	...	...	,,	...	...
3	Basic . . .	...	Dyed	Dyed	,,	...	Dyed
4	Soluble acetate . .	...	,,	...	,,	...	,,
5	Acid chrome . .	...	...	...	...	Dyed	...

The effects indicated are dyeings distinguished from mere tints unworthy of record. Individual dyeings cannot be accepted as indicating a definite dyeing group, but the comparative results of the dyeings may be utilized effectively if due regard is paid to the fact that fibrous materials are rarely dyed with quantities of colour exceeding 10 per cent. of the weight of fibre and frequently not more than 4 per cent. to obtain a full shade. For the purpose of the test the solutions may be boiling. Cold solutions produce little effect in wool dyeing, and a temperature of 80° is more suitable for dyeing acetate silk on account of the delustring which is liable to be effected at the boil, but this does not matter much when dyeing is carried out for the purpose of a test. The soluble acetate colours dye wool in very full shades. It is noteworthy that they also dye tanned cotton.

If it is possible to apply a colour by one of the methods indicated above, the reactions on the dyed fibre may then be carried out quite

rapidly. In addition to the groups already mentioned, relatively colourless or only slightly coloured products, which are soluble in water, may be impregnated on cotton and the colours developed by suitable processes. For this purpose there are available products comprising mixtures of naphthols and stabilized diazonium compounds which yield colours on treatment with acids, for example, rapidogens. These are perhaps more generally used in printing (local dyeing) than in the production of uniform dyeing. Another type of colour requires an acid oxidizing agent for the development of colour. The sulphuric esters of leuco vat dyestuffs which are of the latter type may be padded in the form of aqueous solutions on cotton, or dyed on to wool from an acid bath, giving effects which require oxidation with such oxidizing agents as sodium nitrite and hydrochloric or sulphuric acid in dilute solution. The products which require oxidation are known as indigosols and soledon colours.

Dyestuffs Insoluble in Water

Colours insoluble in water may be tested for solubility in sodium sulphide solution and attempts made to dye cotton in the solution. The sulphur colours dye in this way. Failing to obtain any satisfactory result with sodium sulphide, it is advisable to try the action of sodium hydrosulphite in the presence of a little caustic soda and to discover whether it is possible to dye cotton in the solution so obtained. It is important to observe any colour change which takes place during the process. Sodium hydrosulphite and caustic soda produce yellow solutions with indigoid colours and usually, with anthraquinone vat dyestuffs red, violet or blue vats more intensely coloured than the colour itself. Mordant colours will only dye cotton which has been mordanted with various mineral substances; but it is more convenient to test these colours on wool mordanted with chrome because this is more easily produced.

If a coloured compound is insoluble in water, but on treatment with sodium hydrosulphite and caustic soda yields a solution which will dye cotton, the colour of the reduction product (vat) should be observed and the behaviour of the colour on the dyed cotton after it has been exposed to the air or to the action of a mild oxidizing process should be recorded. Vat dyestuffs in substance dissolve in nitrobenzene, aniline, pyridine, phenol, resorcinol or cresol. It is preferable, however, to test the colours dyed on cotton. A colour may not be a dyestuff but may be intended for use as a pigment in calico printing or for ink or paper making. Insoluble azo-colours, aniline black, ultramarine blue and chrome yellow find application as pigments and may be found on vegetable fibrous material. The insoluble azo-colours and aniline black are produced on the fibre in dyed goods.

Valuable advice regarding methods of ascertaining the constitution of a dyestuff may be obtained from a paper by Fiertz-David (" Analysis of Dyestuffs Yesterday and To-day ")[1] particularly from the description of the use of patent literature and what the author describes as " a mixture of Emil Fischer and Sherlock Holmes " procedure in elucidating the constitution of particular colours.

In considering the identification of insoluble azo-colours on the fibre and of azo-pigments in substance, F. M. Rowe and Clara Levin[2] state that for the purpose of isolating the components of an azo-compound it is often preferable to use one reducing agent for the isolation of one component of a mono-azo-compound and a different reducing agent for the isolation of the other. Sometimes, as for example, from St Dennis Red (a direct cotton colour) the reduction-product obtained is dependent on the agent employed for reduction. This dyestuff which is derived from tetrazotised amino-azo-toluene yields *m*-toluylenediamine when reduced with acid stannous chloride or diamino-azo-toluene with zinc dust and ammonia or diamino-azoxytoluene when carefully reduced with glucose and caustic soda. These workers prepared a large number of insoluble azo-compounds and discovered that it was possible to effect identification by determination of the melting point of a crystallized specimen owing to the large variation in the melting points of isomeric-aryl azo-β-naphthol derivatives and of aryl-azo-β-hydroxynaphthoic acid anilide derivatives. Only a very small specimen is required in a crystalline condition for the determination of the melting point, the coloration in concentrated sulphuric acid and the determination of the elements contained in it. The colours can be extracted from the fibre by suitable solvents and crystallized. It is impossible to give anything like a complete list of all such products which find application in dyeing and printing, but one or two examples will serve to illustrate the principle of this method. The β-naphthol derivative with *o*-toluidine melts at 128°, whilst the naphthol AS derivative melts at 220°; the derivative β-naphthol-6-nitro-*m*-xylidine, m.p. 208° and the naphthol AS, m.p. 289°; β-naphthol-*p*-nitraniline, m.p. 250°; naphthol AS *p*-nitraniline, m.p. 290°.

If the compound is obtained by coupling any diazonium component with any second component, on treatment with cold fuming nitric acid a solution of the diazonium nitrate is obtained. Crystallization and the melting points of the products obtained when half this is coupled with naphthol and half with naphthol AS leads to the identification of the diazonium compound. Examination of the action of fuming nitric acid on a series of azo-compounds indicates whether this is the diazotized amine used in the preparation of the

[1] *J. Soc. Dyers and Col.*, 1929, **45**, 133. [2] *Ibid.*, 1924, **40**, 218.

colour or whether it is a nitro-derivative of that amine. Valuable information leading to the identification of rapid fast printing colours is contained in papers by Rowe and Stafford and Rowe and Corbishley.[1] In this work the rapid fast colour paste is dissolved in water and acidified, a diazonium chloride is obtained and a naphthol, but this being acid the mixture remains without coupling. The naphthol is precipitated and the diazo-compound is in the acid solution. After filtering off the naphthol, one half of the filtrate is coupled with β-naphthol and one half with naphthol AS and melting points are determined. Still further identifications are described.[2] It is not usual for dyers to require such detailed information about the constitution of any dyestuff in substance or on the fibre as this method provides.

Where a large class of dyestuffs of similar constitution is involved, it is always a matter of some difficulty to identify any individual colour and direct comparison with an authentic dyeing is always the most expedient procedure. Small differences in chemical constitution are indicated by the spectroscopic absorption bands, but this involves apparatus and skill which are not at the disposal of many dyers and others interested in the subject of testing colours.

Dyestuffs on Cotton and other Vegetable Fibres

A. G. Green, J. R. Jones, F. G. C. Stephens and G. A. Haley[3] published tables for the identification of colours on cotton and vegetable fibres.[4] The general principles still hold good at the present time, though allowances must be made for the introduction of new dyestuffs and the renaming of dyestuffs. This particularly affects the reducing and reoxidation tests as applied to all vat and azoic colours. Indigoid and many other vat dyes give distinctive colours on reduction in both alkaline and acid media (see pp. 738-9).

Comprehensive tables for the systematic identification of colouring matters of natural and synthetic origin and for the detection of metals in fibrous materials, dyes and organic pigments, have been compiled by E. Clayton.[5]

In these tables, the plan is like that of Green with certain modifications. The solvent properties, alkaline reducing action and moderately high boiling point of commercial ethylene diamine (b.p. 117°) are put to account in distinguishing between vats and azoics in dyeings and prints

[1] *J. Soc. Dyers and Col.*, 1924, **40**, 228 and 230.
[2] *Ibid.*, 1925, **41**, 278. [3] *Ibid.*, 1907, **23**, 252.
[4] These tables appear collectively in the *Manual of Dyeing*, Knecht, Rawson, and Loewenthal.
[5] *J. Soc. Dyers and Col.*, 1937, **53**, 178, 380, and also published as a booklet.

on cellulose fibres, the reduction of vat dyeings being assured by the addition of a little glucose to the ethylene diamine.

Some insoluble azo colours, when dyed on cotton, are destroyed completely, while others may be scarcely affected by reduction with sodium hydrosulphite solution in the presence of alkali. For instance, Paranitraniline Red on β-naphthol is soon decolorised, whereas the blues obtained from Variamine Blue B on Brenthol AS require long boiling with Formosul G (*vide* Clayton's Tables), to which a little caustic soda and hydrosulphite have been added. Acid reduction, such as with titanous chloride, is preferable for soluble azo (direct cotton) colours. The azo-groups are split into amino-groups, which does not always happen with alkaline reduction.

E. Herzog has devised a system for identifying individual vat dyestuffs, which he communicated to the International Association of Colour Chemists in 1932. The tables for the identification of all vat dyestuffs known up to the date of publication were printed in French and German in 1933. The identification of the type of vat dyestuff is established as the result of colour changes produced by three reactions on dyed cotton :—

(1) Concentrated sulphuric acid on a small sample ;
(2) Reduction with sodium hydrosulphite and 2 per cent. caustic soda solution, noticing the effect of warming the solution for a few minutes ;
(3) Acidifying the product of the reaction (2) and observing the change in colour produced with hydrochloric acid on the leuco-compound which acts as an indicator.

The resulting colours are indicated by figures as below :—

0 colourless	5 violet
1 yellow	6 blue
2 orange	7 green
3 red	8 brown
4 carmine	9 grey or black

The colours resulting from each of the three reactions are recorded by their colour numbers in the reverse order to that in which the reactions are carried out so as to give each a three-figure number ranging from 007 to 997. The first figure represents the colour with reaction (3), the second with reaction (2) and the third with reaction (1) above. Thus most vat dyestuffs can be identified as belonging to one or other of the chemical groups :—

Dyestuffs giving colour reactions set out in the table below are described by Herzog (loc. cit.) *and further information may be found there and by reference to the Colour Index* (*F. M. Rowe*) *and* Schultz Farbstoff Tabellen (*VIIth Ed.*), *edited by L. Lehmann.*

No.	Constitution.	No.	Constitution.
007	I	345	...
014	II	347	V
015	II	351	V
016	II	451	VI
017	II	454	VI
018	II	457	VI
023	II	458	VI
026	II	464	VI
027	II	465	VI
057	III	467	VI
110	...	468	VI
111	...	469	VI
116	IV	488	VI
117	...	493	...
121	V	527	V
123	V	557	V
124	V	562	...
125	II and V	565	...
126	II and V	567	...
127	II and V	577	...
131	V	612	...
133	V	617	...
135	V	628	V
137	V	657	...
141	V	661	V
142	V	666	...
143	V	667	V
145	...	668	...
147	...	718	V
151	...	721	V
171	...	727	...
183	...	751	...
184	V	761	V
185	...	770	...
186	...	771	...
187	V	772	...
188	V	777	V
197	V	785	...
198	V	796	V
224	V	835	V
241	...	841	...
242	V	855	...
244	...	864	...
245	V	876	V
251	...	886	...
252	V	898	...
256	V	921	V
257	V	951	...
258	...	957	...
281	V	958	...
284	...	971	...
288	...	981	...
344	...	997	...

I. Derivatives of 3 Indol 2′ Thionaphthen indigo (Ciba red G).
II. Indigoid or Thioindigoid colours (Indigo Thio-indigo red B, Halogen indigoes).
III. Acenaphthenquinone colours (Ciba scarlet G, Helindone scarlet GG).
IV. Carbazol sulphur colours (Hydron blue).
V. Anthraquinone colours (Indanthrene blue).
VI. Benzanthrone colours (Indanthrene dark blue, Benzanthrone violet).

More detailed information is provided by comparing the reactions of the unknown colour dyed on cotton with that of an authentic sample dyeing, which belongs to the chemical group indicated by the tests and is nearest in appearance to it. Confirmation is provided by examining the samples under a quartz analyzing lamp for fluorescence. This test is particularly applicable to Thio-indigoes. It may be used for examining the dry powdered dyestuffs. The test is shown by sulphur colours and thiazols such as Sirius red (see p. 809 *et seq.*).

Yellow to orange vats are produced by the indigoid types I and II. On acidifying, the leuco-compounds become colourless or yellow in the case of indigo and colours of higher molecular weight. The sulphuric acid reactions vary from carmine to blue or green. Ether extracts the leuco-compound from the vat and the colour is again produced by carefully oxidizing the ethereal extract.

Hydron dyestuffs give no yellow colour when spotted with nitric acid.

Indigo and the halogen indigoes differ from one another in the sulphuric acid reaction, but it is not possible to identify them by this means. Some become at first dark olive, then green and blue. The alkaline reduction colour is yellow and with the higher halogenated ones orange.

The decolorization by acid is incomplete in the higher halogenated members.

Nitric acid colours indigo a bright yellow and halogen indigoes pale yellow. The dyestuffs are destroyed and cannot be restored by reducing agents. Indanthrene blue gives a yellow colour, but the blue colour can be restored by reduction with hydrosulphite.

To test for the chlorine or bromine in halogen indigoes, a piece of copper gauze is heated in a bunsen burner until the flame shows no more green colour, and then a sample of the dyeing is burned on the gauze. In the presence of halogen the flame is coloured green again. The test can be applied only to the dyed fabric but not to the dyestuff in substance. Halogenated anthraquinone derivatives show no flame coloration under the same conditions.

G. E. Holden [1] described a ready means of distinguishing many colours and classifying them from the dyeing standpoint. The outstanding feature of this scheme is the use of chloroform for distinguishing insoluble azo and vat (especially indigoid) colours from other colours which do not dissolve and give coloured extracts from the dyed material. This reagent may still be applied with advantage, especially if those engaged in testing apply the chloroform test to insoluble azo and vat dyestuffs of recent introduction to acquire experience with regard to the behaviour of a large number of dyed samples.

[1] *J. Soc. Dyers and Col.*, 1909, **25**, 47.

Titanous chloride is useful for distinguishing between direct cotton, basic, and sulphur colours. Most direct colours (diazo water-soluble colours) are reduced completely and the colour is destroyed by this reagent. The basic colours become yellow or orange and either on the fibre or in the solution the colour is restored by air oxidation (Azine, Thiazine, Oxazine) or by the action of a small quantity of an oxidizing agent (triphenylmethane dyestuffs). The test for restoration of colour may be carried out with a few drops of ferric chloride or a very dilute solution of hydrogen peroxide. If the latter is used the action must be observed with care so that over-oxidation is avoided. Green recommends a 2 per cent. solution of ammonium persulphate. The two classes of colours which give coloured extracts with chloroform are vat and insoluble azo colours. Sometimes these extracts are characteristic. Indigo gives an intensely blue chloroform extract even with a light dyeing. Indigo derivatives such as Ciba blue 2B, Durindone colours, and dyeings of Indigosols show intense colorations. The Caledon and Indanthrene colours show less solubility, but some of them give a solution with characteristic fluorescence. Indanthrene dark blue gives a bluish-green colour with red fluorescence. In the case of blue colours it is the vat colours which yield most characteristic chloroform extracts, but in the case of red colours, it is the insoluble azo colours which give the most characteristic effects. Para red gives coloured extracts which appear very intense for many successive extractions. The Naphthol AS colours also show strong colorations. The hydrosulphite or vatting test is generally effective in distinguishing between colours which are extracted by chloroform. The vat colours behave as previously described while the azoic colours are either completely destroyed or may be extremely resistant to attack unless some catalytic substance such as anthraquinone is added to the reducing agent. The naphthol AS red corresponding to para red leaves a yellow residue on the fibre after reduction and this is not oxidized back to the dyestuff. Dyeings which have been proved by the chloroform test to be something other than vat and insoluble azo or azoic colours are next tested with titanous chloride. Such colours as benzopurpurine first turn blue owing to the presence of hydrochloric acid in the titanous chloride and on boiling the solution, the colour of this and many other direct colours is completely destroyed. A number of yellow colours remain yellow, while some browns and reds are changed to yellow. If the colour remains yellow when attempts are made to restore the original colour by the addition of an oxidizing agent, it is best to attempt diazotizing and developing with β-naphthol. The production of a red indicates Primuline or some colour of which primuline forms the base. Many direct colours yield an extract with boiling water from which it is possible

to transfer the colour to ordinary or mercerized cotton. This test may present a certain amount of uncertainty with some of the faster direct cotton colours, especially when they are dyed in very light shades on mercerized cotton or on viscose. Fortunately the colour of such dyeings is easily destroyed by reduction, so they are not confused with other groups.

An aqueous solution of pyridine dissolves direct colours.[1] It is asserted that when dilute pyridine (15 to 20 per cent.) is coloured more strongly than dry pyridine, a direct colour is indicated. In most cases dry pyridine gives no extract with direct colours. Logwood on iron, chrome or copper mordant gives a pale red or brownish red extract, but this colour is easily identified by the red colour which it gives with hydrochloric acid and by the presence of mineral substances in the residue after ignition. When dry pyridine is coloured more strongly than aqueous pyridine a direct colour is not present but a vat colour is indicated and should be tested for, as previously described. The solubility of vat dyestuffs in pyridine has long been known. In the tables for the identification of vat dyestuffs published by M. Vajs [2] there is included a test with pyridine in which 76° Tw. caustic soda is afterwards added to the pyridine extract, so that the pyridine layer rises above the caustic soda and the changes in colour of fibre and solution can be observed more conveniently.

In testing for reoxidation, such as occurs in the case of basic colours reduced by titanous chloride, both fibre and solution should be tested, as the colour is often removed from the fibre by the acid solution and some may be regenerated on the fibre and some in solution. Basic colours are soluble in alcohol and are dissolved from most fibrous materials by alcohol. The colour of the extract should be observed. A fluorescent extract indicates a colour of the Rhodamine type. On adding water to the alcoholic extract and placing in the solution a small sample of white cotton yarn and one of tanned cotton yarn, the tanned cotton is the more deeply stained if the original sample was dyed with a basic colour (Methylene blue, Magenta, Malachite green, Bismarck brown and Acronol colours). The test can be carried out with a very small extract and is useful in detecting basic colours in dyeings where more than one colour has been applied. Alkalis such as 10 per cent. caustic soda solution dissociate the colour base in the dyed fabric. The colour bases are soluble in ether and can be identified by evaporating the ethereal extract and moistening the residue with acetic acid ; the acidified solution dyes tanned cotton better than white cotton yarn if a basic colour was present in the original dyeing.

Titanous chloride reduces the colour of dyeings of sulphur colours

[1] Zühlke, *Mell. Textilber.*, 1936, 17, 866. [2] *Textilber.*, 1927, p. 611.

to yellow or brown, which may be reoxidized with restoration of the original colour on the fibre, if the sample is exposed to the air for some time or more rapidly by the cautious application of an oxidizing agent such as ammonium persulphate, dilute hydrogen peroxide or ferric chloride. Ferric chloride is very useful in testing for the reoxidation of colours, which are liable to be completely destroyed by more powerful oxidizing agents. During the reduction with titanous chloride a piece of filter paper, on to which has been spotted a solution of lead acetate, should be held over the top of the test-tube to form a lid. A black stain indicates the presence of a sulphur colour. Having observed the behaviour of the colour to alcohol, in which sulphur colours are insoluble, the sulphuretted hydrogen test is reliable. For the reduction test it is important to use a sufficiently dilute solution of titanous chloride, and to avoid much hydrochloric acid in the solution. In this test it is most important to realize that the identifications are in some cases micro-tests.

The following tests recommended by Green are applied with advantage after the chloroform test and when no extract is obtained with that solvent :—

Colours stripped from cotton by weak ammonia (1 : 100)

Persian berries on Tin mordant.
Quinoline yellow. Eosine orange.
Indian yellow Orange IV G, etc.
Crocein scarlets.
Soluble and alkali blues.
Coomassie violets.
Acid greens.
Fast brown.
Naphthylamine brown.
Naphthol blacks.

Colours stripped by saline caustic soda boiling for half a minute, rinsing and boiling twice in weak formic acid (1 : 100)

Chrome yellow and orange. (Test with ammonium sulphide, colour blackens.)
Alizarine yellow A (azo alizarine colour).
Thioflavine T.
Auramine.
Chrysoidine.
Acridine yellow and orange.
Acronol colours.
Rhodamine.
Saframine.
Magenta.
Anisoline.
Methyl violet.
Gallocyanine.
Chrome violet.
Methylene blue.
Indoine.
Victoria blue.
Chrome blue.
Methylene green.
Brilliant green.
Chrome green.
Bismarck brown.
Indanthrene yellow G is reduced and becomes blue if any oxycellulose is present and with ordinary cotton on persistent boiling.

Colours stripped by hydrochloric acid (20 *per cent.*) ; *the stripped solution is red*

Tannate of iron. Logwood on Fe. Logwood on Cr.

Direct colours which have been after-treated by various processes to improve their fastness may resist the bleeding test, but are generally readily reduced. The confirmatory test with aqueous pyridine is recommended. Up to the present there do not appear to be any infallible tests for certain types of after-treatment. For example, the test which consists in incinerating the sample, moistening with concentrated nitric acid, evaporating almost to dryness, taking up with water, filtering and rendering alkaline with ammonia, when a blue colour should be observed if copper is present, may fail in testing coppered direct colours. Even more delicate tests for copper have failed in testing coppered direct colours. The only satisfactory method in these cases is to compare with authentic samples of likely type and colour, having regard to the particular type of fastness which any after-treatment is claimed to yield, and general similarity of behaviour towards acids and alkalis.

The mordant dyestuffs, of which Turkey red is the most important if cotton is considered, show no solubility in chloroform and are very fast to both dilute acids and alkalis. Turkey red is dissolved by cold concentrated sulphuric acid with a beautiful red colour which on pouring into water becomes yellow. If to this solution caustic soda is added in excess, the solution becomes violet. A Turkey red gives a white ash on incinerating the dyed fibre. The colour is destroyed by a solution of 5° Tw. bleaching liquor containing 1 drop of glacial acetic acid, but it is not destroyed by 5° Tw. bleaching liquor without acid or exposure to air. To detect the alumina in a Turkey red it is of little use to apply the ordinary test with ammonia, but even in a Turkey pink the alumina may be found in the fibre on which the red has been destroyed with bleaching liquor and acetic acid, if the material is well washed with water and placed in a decoction of logwood extract in a test-tube. On boiling for a few minutes and removing the fibrous material and washing, it will be dyed violet if alumina is present.

Most of the mordant dyestuffs in use at the present time are either applied to wool or in the printing of cellulose materials. Chromium and occasionally iron are the metallic mordants used and as some mordant is essential for obtaining the colours, the presence of these metals in the dyed fibre is a definite indication (in conjunction with their resistance to dilute boiling acids and alkalis and non-solubility in chloroform) of the presence of mordant dyestuffs. It is best to incinerate the dyed material and to apply the chromate test. The usual ferrocyanide test may be applied for iron in the ash. A mordant dyestuff which still finds some application in dyeing and occasionally appears on both cotton and wool is logwood. It has been recently recommended for acetate silk goods. The black is turned red by a drop of concentrated hydrochloric acid, or brown if chromium

is present; ammonia restores the original shade. Either iron or chromium can be easily detected, and sometimes copper is also present and in this connection is not difficult to detect. Aniline black resembles sulphur black in its reactions, but does not evolve sulphuretted hydrogen when boiled with titanous chloride. It is much more resistant to hypochlorites than the latter, but it is eventually turned brown, especially if a little acetic acid is present. The ash may contain chromium (aged or dyed black) or iron (steam or prussiate black). A diphenyl black contains no chromium. A red colour of the saffranine class is extracted from aniline black by alcohol containing a little acetic acid. The extract dyes wool and tanned cotton and is turned blue by nitrous acid. If black cellulose material is treated with concentrated sulphuric acid, poured into water, a pale green colour indicates aniline black, or, if the solution is colourless, a sulphur colour. On boiling with concentrated caustic soda solution, sulphur blacks yield a grey-blue to steel-blue colour. The sulphur colour Indocarbon CL is remarkable for its good fastness to chlorine, and as this colour is claimed to be a non-tendering dyestuff its distinguishing property in respect to chlorine is of interest as a test. The colour is dissolved by sodium sulphide solution.

Pigment Colours. Lead chromate is stripped by boiling caustic soda, the yellow is blackened by ammonium sulphide. The ash of the dyed material contains lead and chromium.

Iron Buff and Mineral Khaki. The ash contains iron and in the latter case chromium. The colour is unaffected by boiling 10 per cent. caustic soda, but is stripped by dilute hydrochloric acid, and both fibre and solution turn blue with potassium ferrocyanide. The colour is darkened to slate grey with tannic acid. It is not affected by bleaching liquor. The dyed material may be tested for chromium by boiling with dilute caustic soda solution and a little hydrogen peroxide. The chromium on the fibre is converted into soluble lead chromate, and on acidifying and cooling well and adding ether, the ether becomes coloured blue.

The fixation of pigment colours such as ultramarine is carried out in printing by entanglement in a coagulum of albumen or by means of a deposit of cellulose material on the fabric. The same methods are applied in the fixation of organic pigments derived from azo colours, etc. Albumen is dissolved in caustic soda and the pigment is then disengaged from the fabric. Ultramarine is easily affected by heating with hydrochloric acid, when it gives off hydrogen sulphide. The organic pigments are dealt with by treatment with concentrated sulphuric acid and pouring into water, being afterwards tested by the methods previously described. Concentrated sulphuric acid will also bring about the removal of cellulose material and release the coloured

compound. Acetate cellulose which may be used for fixing pigments can be dissolved off the fabric with acetone, thereby releasing the pigment.

Cutch brown darkens with ferric iron solutions. The colour is lightened by bleaching liquor (5° Tw.). The fibre may be tested for copper and chromium.

One of the most interesting features of Clayton's work dealing with the detection of metals is the use made of the liberation of sulphuretted hydrogen by the addition of hot and concentrated formic acid to a solution of sodium sulphoxylate formaldehyde, the lower sulphides of mercury, lead, copper, cadmium, arsenic, and antimony are precipitated if the corresponding metals are present, without deposition of finely-divided sulphur. It is claimed that 1 part arsenic in 2,000,000 and 1 part copper in 1,000,000 may be detected.

Dyestuffs for Cellulose Acetate

The identification of dyestuffs on cellulose acetate may be a very difficult matter because single colours are not frequently used. C. M. Keyworth[1] points out that it is well known that dyeings of different strengths of the same dyestuff may give somewhat different reactions. Thus a dyestuff which is stripped by hydrosulphite in light shades may be stripped only with difficulty in dark shades. Dyestuffs are more readily stripped from yarn than from piece goods. Mordant colours are rarely used on cellulose acetate, but in mixed fabrics they may be found on the other fibrous material. Vat dyeings are not used unless the fibre has been hydrolysed, but vat prints are common and easily identified in the same way as on cotton. In order to effect penetration it was found necessary to apply other reagents than those recommended by Green for cotton. Hydrosulphite B, a reagent which easily decolorizes dyestuffs on cotton, will not do so on acetate silk. Hydrosulphite RS, containing hydrosulphite, Rochelle salt, and caustic soda, is useful for dyestuffs of the anthraquinone series, and titanous thiocyanate has been found extremely useful in giving indications of constitution when hydrosulphite B and RS fail to do so.

Basic colours are stripped with 5 per cent. acetic acid and are reduced by titanous thiocyanate, but the colour returns on treating colours of the triphenylmethane series with hydrogen peroxide. The direct colours are little affected by boiling alcohol, but diazotized and developed colours (Cellitazoles) are stripped. They are only slightly affected by boiling with acetic acid, but hydrochloric acid often changes the shade. They are only slightly stripped by ammonia.

[1] *J. Soc. Dyers and Col.*, 1927, **43**, 346.

The following reagents are useful in testing colours dyed on acetate silk :—

94 per cent. alcohol.

5 per cent. acetic acid : The sample is boiled for half a minute.

100 ml. concentrated hydrochloric acid diluted with 900 ml. water : The sample is boiled for 1 minute.

1 per cent. ammonia : The sample is boiled for 1 minute.

Saline caustic soda (900 ml. 80° Tw. caustic soda is mixed with 100 ml. saturated common salt solution) : The sample is boiled for 1 minute, or till decolorized.

Hydrosulphite B : 100 g. hydrosulphite NF in 1 litre water is acidified with acetic acid—only of general interest.

Hydrosulphite BX : 100 g. hydrosulphite NF and 2 g. precipitated anthraquinone are dissolved as recommended by Green in 1 litre water slightly acidified with acetic acid. Cellulose acetate silk is stained yellow on boiling with this solution and it is consequently difficult to obtain indications with orange and yellow colours.

Hydrosulphite RS : 100 g. hydrosulphite NF, 50 g. Rochelle salt, 50 ml. caustic soda, 80° Tw. and 800 ml. water. Colours of the anthraquinone series which are unaffected by hydrosulphite BX are decolorized giving coloured extracts. Saponification of the cellulose acetate occurs and materially assists the reduction of the colour.

Titanous thiocyanate : A 20 per cent. solution is used and can be stored in a stoppered bottle. Owing to the dark colour of the solution, the reduction cannot be observed. The solution containing the sample is heated to boiling, boiled for 1 minute. The sample is rinsed, brought to the boil in fresh water, and hydrogen peroxide added to ascertain whether reoxidation has occurred.

Hydrogen peroxide : For reoxidizing leuco-compounds. After reduction the sample is rinsed, brought to the boil in fresh water, and a few drops of slightly acidified 10 vol. hydrogen peroxide added. Some basic colours require acid oxidation after hydrosulphite RS for restoration of colour.

Chemic 4° Tw. : Acidify with 4 ml. glacial acetic acid per litre. 4° Tw. chemic at *p*H 7 leaves many dyestuffs unchanged, but addition of acid brings about decolorization.

The following table gives the general properties of the three important groups to which many acetate silk colours belong :—

Reagent.	Basic.	Azo.	Anthraquinone.
Alcohol.	Str. or sl. str.	Sl. str.	Str.
5 per cent. acetic.	Str. or sl. str.	L.C.	L.C.
1 per cent. ammonia.	L.C.	L.C. or sl. str.	L.C.
Dilute HCl.	Sl. str.	Vary.	L.C.
Saline caustic	Str. Many return with acid	Vary.	Consid. C.
Hydrosulphite BX	Mostly decol. R.W.P.	Decol. D.N.R.P.	L.C.
Hydros. R.S.	Decol. R.W.P.	Decol. D.N.R.P.	Decol. D.N.R.P. col. extract.
Titanous thiocyanate	Decol. R.W.P.	Decol. D.N.R.P.	Decol. (pale yellow) D.N.R.P.
Conc. acids.	Lighter.	Darker.	Lighter.

Sl. = slightly ; str. = stripped ; consid. = considerably ; L.C. = little change ; R.W.P. = returns with peroxide ; D.N.R.P. = does not return with peroxide.

Constitution of the Colours

Cellutyl colours	Are of the basic, azo and mordant types.
Cellatine	Of the anthraquinone series.
S.R.A.	Azo (Golden yellow X, Golden orange I, II, and III) anthraquinone colours.
Cetacyl	Basic colours.
Cetacyl direct; Cebacet and cellito . .	Azo.
Cellitazils	Include organic bases to be diazotized and developed on the fibre.
Celliton; Celliton fast	Anthraquinones.

A very comprehensive series of tables is given by Keyworth.[1]

It is evident, however, that when compounds which are used for dyeing acetate silk belong to such well-known groups as basic colours the usual tests with tanned cotton and attempts to transfer the colours to other fibres are suitable methods of attacking the problem of discovering the type of colour.

Dyestuffs for Wool and other Animal Fibres

The reactions previously described are in the main applicable to wool with very little variation. As a general rule, colours are more resistant to treatment on wool than the same colours dyed on cotton. Leuco-compounds remain attached to the fibre after the colours have been reduced. In slightly alkaline solution the split-products of azo dyestuffs are completely removed from wool. Green states that the reactions on dyed wool are sharper than when the colours are tested in substance.

Vat mordant and naphthol colours are not stripped either by ammonia or by acetic acid. Mordant colours on wool resist the action of sodium hydrosulphite. They usually contain chromium, which will be found in the ash of the incinerated wool.

The following reagents are required :—

Dilute ammonia : 1 : 100.
Aqueous alcoholic ammonia : 1 ml. conc. ammonia, 50 ml. alcohol, 50 ml. water.
Dilute acetic acid : 5 ml. glacial acetic, 95 ml. water.
Dilute alcohol : 50 ml. P.B.S. to 50 ml. water.
Dilute hydrochloric acid : 1 conc. acid, 10 ml. water.
Caustic soda : 10 per cent. solution.
Hydrosulphite A : 10 per cent. formaldehyde compound of sodium sulphoxylate.
Hydrosulphite B : Prepared by acidifying 250 ml. solution A with 1 ml. glacial acetic acid.

[1] *J. Soc. Dyers and Col.*, 1927, 43, 346.

Hydrosulphite AX: Dissolve 50 g. hydrosulphite NF or its equivalent in 150 ml. hot water at 90°, add to the hot solution 0·25 g. precipitated anthraquinone, previously ground to a fine paste, and dilute to 500 ml. with cold water.

Persulphate: A cold saturated solution of potassium persulphate or a 1 per cent. solution of ammonium persulphate. If the solution is alkaline it is neutralized with dilute acid.

Sodium acetate: 5 per cent. solution.

A. G. Green, H. Yeoman and J. R. Jones[1] published tables for the identification of colours on wool.

Colours stripped by 5 per cent. Acetic Acid—Extract Dyes tanned Cotton.[2]

Phosphine.
Benzoflavine.
Auramine.
Thioflavine T.
Chrysoidine.

Acronol Colours.

Basic red dyestuff.
Pyrone group dyestuffs.
Azine group dyestuffs.
Triphenyl methane group.
Soluble red woods.
Basic violet.
Methylene blue.
Indoine.
Victoria blue.
Night blue.
Diamond green.
Azines—Fast green M.
Malachite green.
Bismarck brown.
Diazine black.

Colours stripped by Dilute Ammonia 1 : 100

Coomassie Colours.

Quinoline yellow.
Tartrazine.
Naphthol yellow S.
Fast yellow.
Metanil yellow.
Eosine.
Acid eosine.
Rosindulin.
Acid magenta.
Fast acid violet.
Acid violet.
Soluble blue.
Patent blue.
Wool blue.
Indigo carmine.
Prussian blue.
Lanacyl blue.
Alizarine blue.
Azine green.
Acid green.
Acid brown.
Fast acid brown.
Naphthol black.
Naphthylamine black.

Some of the azo acid colours such as Polar brilliant red 3B are reduced completely with titanous chloride and by hydrosulphite. These colours possess excellent light fastness.

While nitro-, nitroso- and azo- compounds are completely destroyed on reduction, Green observed that those dyestuffs having an ortho-quinonoid structure gave leuco-compounds which were readily reoxidized by air to the original dyestuff and those to which a paraquinonoid structure is attributable gave leuco-compounds stable

[1] *J. Soc. Dyers and Col.*, 1905, **21**, 236.

[2] Basic colours are only used to a small extent in wool dyeing, but are largely used on silk.

to air but reoxidized by oxidizing agents. Generally the leuco-compounds obtained on the wool fibre with sodium hydrosulphite are retained by the fibre, but the reduction products of azo dyestuffs are removed by washing.

Decolorised by hydrosulphite.			Not altered by hydrosulphite.	Not decolorized but changed in shade.
Colour restored on exposure to air.	Colour restored by oxidation.	Colour not restored.		Colour restored by air or persulphate.
Azines Oxazines Thiazines Indigoids	Triphenylmethane	Nitro Nitroso Azo ...	Pyrone Acridine Quinoline Thiazol Some anthracene colours	Most anthracene colours ...

The reoxidation of leuco-compounds oxidizable by air is often accelerated by ammonia vapour. If air does not restore the colour a little potassium or ammonium persulphate solution is added. Safranine and its azo-derivatives, *i.e.* indoine, yield a violet colour on reoxidation if the formaldehyde compound of hydrosulphite has been used as the reducing agent.

Some of the most useful reagents for testing colours on dyed fabrics and the indications which they give are shown in table below.

Reagent.	Action.	Type of colour indicated.
1. Water with white cotton present and boiling	Coloured extract, cotton stained or slightly stained	Direct colour Basic colour possible
2. Chloroform . . .	Coloured extract	Insoluble azo colours. Vat colours
3. Sodium hydrosulphite + caustic soda (applied when chloroform test is positive)	Colour destroyed. Colour altered, *e.g.* turned yellow but restored by oxidation. Characteristic vatting	Insoluble azo colours (see text) Indigoid Indanthrene and other vat colours
4. Alcohol	Coloured extract	Basic colours
5. Titanous chloride (applied when chloroform test is negative), 25 c.c. (20 per cent. commercial) $TiCl_3$ and 25 ml. HCl per litre water	Colour destroyed. Turned yellow, but can be rediazotized and developed. Turned yellow, H_2S evolved, colour restored by oxidation No H_2S evolved	Direct and acid colours Primuline and developed Sulphur colour Basic
6. Bleaching liquor, 5° Tw. + 1 drop acetic	Colour destroyed only on addition of acid. Test for alumina by dyeing logwood. Test for chromium	Turkey red and other mordant colours Cutch Logwood

Clayton finds that some of the fastest co-ordinated lakes on wool, *e.g.* the chromium lake of Eriochrome Black T Supra and all the Neolan colours, are dissolved from wool by ethylene diamine even in the cold if allowed to stand for some time. The group reducing agent for wool is Formosul G, which consists of 20 g. Formosul dissolved in 75 ml. hot water and diluted with 75 ml. cold water and 50 g. ethylene glycol.

Mixtures of Dyestuffs

Very few of the commercial artificial dyes consist of pure colouring matters, but in the majority of cases the dye as sold will be found to contain a considerable percentage of mineral salts, such as sodium sulphate, sodium chloride, sodium phosphate, sodium carbonate, and organic substances such as dextrin. These substances are not present as adulterants, but have been added for purposes of standardization, since it is not commercially practicable to manufacture successive batches of a given dyestuff that will have exactly the same tinctorial strength or purity of shade. The dyestuff content or colour value is adjusted by the addition of the diluents mentioned above, until it matches the " type " colour, and the shade is corrected, when necessary, by the addition of small amounts of other dyestuffs of a similar class. In some cases the desired shade of a dye will be produced by making a deliberate mixture of pure dyes of complementary colours. Thus a much used " Neutral Grey " will be found on careful examination to be composed of a mixture of a red, a blue and a yellow dye.

When it is required to know whether a dye is a mixture or not, if the mixture has been prepared by merely grinding the constituents together, a very small quantity of the powder is taken on the end of a knife-blade, and blown so as to scatter it over the surface of cold water in a large porcelain basin, on to the surface of a wet filter paper or on to wet calico which is more useful for mounting. Each particle of dye will reveal itself as a coloured streak as it dissolves. A mixture may sometimes contain two dyes of very similar colour in aqueous solution, but with different chemical constitutions, or the dye powder may be insoluble in water. Under these conditions, useful information may often be obtained by sprinkling the powder on to the surface of concentrated sulphuric acid in place of water.

Clayton describes the application of a chromatographic method of adsorption for the separation of two or more colours in solution obtained from mixed dyeings. A creamed mixture of Brockman's aluminium oxide (Merck's product) and a solvent is introduced into a small tube attached to a flask with connections which enable the dye solution to be drawn through the aluminium oxide by slight

suction. The adsorbent mixture undergoes elutions and re-adsorptions from particle to particle, thereby causing individual dyestuffs to pass down at different rates. The process may be used with water, ether or chloroform as solvents, and alcohol, pyridine or acetone for elution.

Although it is unsatisfactory to indicate any exact details of procedure to be adopted in identifying mixtures of dyestuffs either in substances or on the fibre, it will be realized that the foregoing tests may be adapted for such identification. In the case of dyestuffs of different groups it is only certain members which are likely to appear in admixture and these colours usually exhibit their diverse composition at once. Colours of the same class very rarely show the same ease of reduction and oxidation, so that by careful treatment, in what may be described as restricted oxidation and reduction tests, two or more colours may be observed. For example, a dyeing of the direct colours chrysophenine and chlorazol sky blue producing a green is changed to blue by titanous chloride before the complete destruction of the colour, and to a yellow with 5° Tw. bleaching liquor. The yellow remains on oxidation for some time after the blue is destroyed.

In his admirable system, Clayton claims no more than a dyeing or chemical group classification for the colours under test and refers those who wish for more detailed information or individual identification to the special reactions given in the Colour Index. However, it is generally recognized that the ability to spot particular dyestuffs depends upon somewhat extensive experience of the appearance and behaviour of colouring matters, especially under the influence of reducing and oxidizing agents. This experience may be assisted by such data as that supplied by Herzog, but it appears that more than one reducing agent may be necessary for the identification of individual dyestuffs. Thus Ferraris [1] has found it necessary to supplement the vat dyestuff testing tables of Herzog by tests with stannous chloride and nitric acid (1·4-1·45 sp. gr.).

Reichenstein [2] recommends a molten mixture of urea and stearic acid for determining the acidic character of organic dyestuffs in micro-quantities; traces of basic dyestuffs colour the stearic acid which separates in the upper layer and acid colours tint the urea (lower layer).

VII. QUANTITATIVE ESTIMATION OF DYESTUFFS

By Eva Hibbert, M.Sc. (Tech.)

A. Dye Trials

Dye trials do not admit of the same accuracy as a chemical method such as reduction with titanous chloride, but have been

[1] *Rev. Gén. Tein. Imp. Blanch.*, 1937, 15, 411 and 539. [2] *Helv. Chim. Acta*, 1937, 20, 882.

largely employed in practice because with careful adaptation they are capable of providing a convenient comparison with recognized standard dyestuffs. In some cases, a dye trial is advisable even after the actual reducing value has been obtained, because very small additions of an admixed dyestuff may modify the shade obtained in dyeing. From 0·5 to 1 per cent. of colouring matter on the weight of material, or 10 per cent. in the case of pastes, is a convenient amount to use. Much time would be wasted in weighing out such small quantities of dyestuff, so that it is both more convenient and more accurate to weigh out, say, 5 g. of dye and make it up to 500 ml. in water, this giving a 1 per cent. solution ; pastes are made up to 10 per cent., from which the required amount is taken by means of a pipette or small measuring cylinder. Assistants such as Glauber's salt and sodium chloride are best kept in the form of 10 per cent. solutions ; acids, sodium nitrite and soap at 1 per cent. strength.

It is advisable to use only freshly prepared solutions of dyestuffs, since many of them undergo a gradual decomposition when kept for any length of time in dilute solutions. When a fresh delivery of dye has to be tested against the standard, it is always necessary to make a dye trial of the standard at the same time, thus ensuring that the dyeing conditions are alike for the two dyes. Many dyestuffs, too, alter in shade on keeping. Benzo-purpurine 4B, for instance, goes darker, through the action of the acids in the atmosphere. For basic dyes it is better, for a similar reason, to use a freshly mordanted lot of cotton hanks, which have all been mordanted in the same solutions, since the behaviour towards the dyes, of yarn that has been mordanted and dried off is not quite the same as that of yarn that is dyed directly after mordanting, and has not had a preliminary drying. Similar precautions should be taken when applying naphthols. The preparing should be done with a freshly made solution of the naphthol, and the same used for the sample as for the standard. The method is applicable to the comparative valuation of tannic acid. When comparing a new brand of dyestuff against the standard, dyeings of each should be made at 0·5, 1 and 1·5 per cent. Should the new dyestuff show a difference in depth as compared to the standard, additions of further amounts of dye solution can be made to the weaker baths until an approximate match is obtained. Such a procedure will not give accurate results. To obtain an exact valuation of the new dye, a second set of dyeings must be carried out with an alteration in the initial amounts of dye taken, which is calculated to give a close approximation to the true value, and, if necessary, a third test is made, until an exact match is arrived at. The tinctorial value of the two dyes will then be inversely proportional to the amounts taken to obtain the match.

Valuable information can also be obtained by making dyeings proportional to the price per pound of the samples. Thus, if a new dyestuff is being offered at 2s. 6d. per lb. as against the standard at 3s. 6d., dyeings should be made in the proportion of 30 of the standard against 42 of the new sample, or 5 of standard to 7 of the new dye. That is to say, one would make dyeings of the standard at 0·5, 1 and 1·5 per cent., against 0·7, 1·4 and 2·1 per cent. of the sample. If the three pairs of dyeings match each other, it may be concluded that the new dye at 2s. 6d. has the same money value as the standard at 3s. 6d. Should differences be apparent after drying up, a second set of dyeings with the estimated adjustments will show the real money value of the new sample. When comparing two dyes that do not exhaust well, it is quite possible that though they may give identical colour values at the first dyeing, the residual liquors may behave quite differently. To investigate this point the residual liquors are made up again to their original volumes with water alone, and a fresh set of dyeings made. If any colour still remains in the baths, a third set of hanks should be put through and the colour of these carefully compared with the first set for quality of shade. The depth of tone will naturally be much less than in the first patterns.

These tests will show whether, in a dyestuff mixture, the standard and sample are identical in composition. This point is especially important where large quantities of material are to be dyed to the same shade, and the colour does not exhaust. The dyeing has then to be carried out from a standing bath. That is to say, after each lot of material has been dyed, the liquor is adjusted to its original volume, and fresh quantities of assistant and dyestuff are added in such proportions as will compensate for what was removed during the previous dyeing operation.

If the exhaust tests show differences between the first and subsequent dyeings, it indicates that there will be trouble in keeping successive dyeings up to shade.

The dye trial method may be applied to dyestuffs of any group and may be adapted for naphthols if the appropriate method of application is carried out with a standard for comparison with the specimen to be evaluated.

B. Chemical Methods

These may be classified as follows :—

1. Precipitation. 2. Oxidation. 3. Reduction.

1. Precipitation Methods

Precipitation of one colour by another and by means of an alkaloid has been the basis of several analytical processes. For example,

Rawson [1] utilized a standard solution of night blue for precipitating naphthol yellow S and some acid (azo) dyes.

10 g. night blue and 50 ml. acetic acid are dissolved in water and made up to 1 litre. 10 ml. is measured into a conical flask and about 30 ml. naphthol yellow S (0·1 per cent. solution) is run in from a burette. The mixture is well shaken and poured on to a filter paper. Another experiment is made with a smaller quantity of yellow, if the filtrate in the first case is of a distinct yellow colour. If the filtrate is blue or colourless, more of the yellow solution is required. Experiments are made until the solution obtained is faintly yellow. By spotting on filter paper and observing the colour of the halo formed round the precipitate it is possible to reduce the number of filtrations very materially. The night blue may be standardized by means of a crystallized sample of naphthol yellow S. 1 g. commercial night blue precipitates 0·25 g. pure dry naphthol yellow S. It is accepted therefore that 2 mols. night blue combine with 1 of naphthol yellow S.

A Seyewetz [2] applied the principle to the estimation of a number of colouring matters. Kay and Appleyard [3] used night blue precipitation for the estimation of picric acid. They found that 1 mol. of night blue precipitated 1 mol. of picric acid and obtained a similar result with crystal violet and picric acid. As it appears that two nitro-compounds like picric acid and naphthol yellow give precipitates in which the components are in different proportions and for some colours the proportions have never been definitely ascertained, the applicability of this method is limited from the point of absolute standardization. Moreover, it is somewhat tedious to ascertain the end-point in the precipitation.

S. R. Trotman and T. B. Frearson [4] make use of the insoluble salts which are formed by alkaloids and complex acids. Certain dyestuffs containing sulphonic groups behave in a similar way. Direct dyestuffs and neutral dyeing acid dyestuffs give precipitates with excess of alkaloid salts. Acid dyestuffs which dye from a dye-bath containing sulphuric acid are not precipitated, or are only incompletely precipitated. The direct colours form compounds such as chrysophenine with cinchonine $C_{30}H_{26}N_4O_2(SO_3H)B_2$, diamine sky blue $C_{34}H_{24}N_6O_4(SO_3H)_2B_4$. 0·1 to 0·2 g. of the dyestuff is dissolved in water, the solution filtered and a cold saturated solution of cinchonine sulphate is added little by little until no more precipitate is formed. The mixture is allowed to stand three to four hours and filtered on a weighed Gooch crucible, the precipitate washed with a cold saturated solution of cinchonine sulphate, dried at 105° and weighed. The

[1] *J. Soc. Dyers and Col.*, 1888, **4**, 82.
[2] *Rev. Gén. des Mat. Col.*, 1901, **5**, 44 ; *J. Soc. Chem. Ind.*, 1901, **20**, 384.
[3] *J. Soc. Dyers and Col.*, 1888, **4**, 83.
[4] *Ibid.*, 1931, **47**, 344.

solubility of cinchonine sulphate at 15° is 1·3 per cent. and when the asbestos mat is washed with the reagent before use, the error is negligible, affecting only the third place of decimals.

2. Oxidation Methods

These were applied most successfully to the analysis of indigo at a period when natural indigo had to compete with the newly introduced synthetic product. C. Rawson [1] describes the process of estimating indigo in the form of an aqueous solution of the sodium disulphonate by oxidation with potassium permanganate.

0·5 g. powder indigo is intimately mixed with its own weight of powdered glass. This is added with constant stirring to 20 ml. of concentrated sulphuric acid and the mixture heated to 70° for three-quarters to one hour. The product is poured into water and made up to 500 ml. 25 to 50 ml. is diluted in a large evaporating dish with 300 ml. of water and the dilute solution titrated with $N/50$ potassium permanganate (0·632 g. per litre). The end of the reaction is marked by a change in colour from blue to yellow in pure indigotin and the better qualities of indigo. Samples of commercial indigo as at present manufactured give satisfactory end-points in titrating and there is no need to adopt any of the processes which were introduced when the permanganate method was applied to the analysis of natural indigo. Such methods are fully described in the *Manual of Dyeing* (Knecht, Rawson and Loewenthal). Only the tetrasulphonate method need be referred to in the present work. In W. P. Bloxam's tetrasulphonate process 1 g. indigo is weighed into a small spouted beaker, 5 ml. fuming sulphuric acid added, and the mixture stirred with a glass rod. It is heated in the water-oven for half an hour and subsequently diluted to 500 ml. 100 ml. is mixed with 80 ml. of a solution of potassium acetate containing 450 g. per litre. A precipitate is formed, but this is dissolved by heating. The solution is cooled in ice water and the tetrasulphonate which crystallizes out is filtered off on a Gooch crucible and washed with an ice-cold solution containing 225 g. potassium acetate and 12·5 ml. glacial acetic acid per litre. The precipitate is dissolved and made up to a known volume. The solution may be titrated with either potassium permanganate or titanous chloride (see p. 760).

3. Reduction Methods

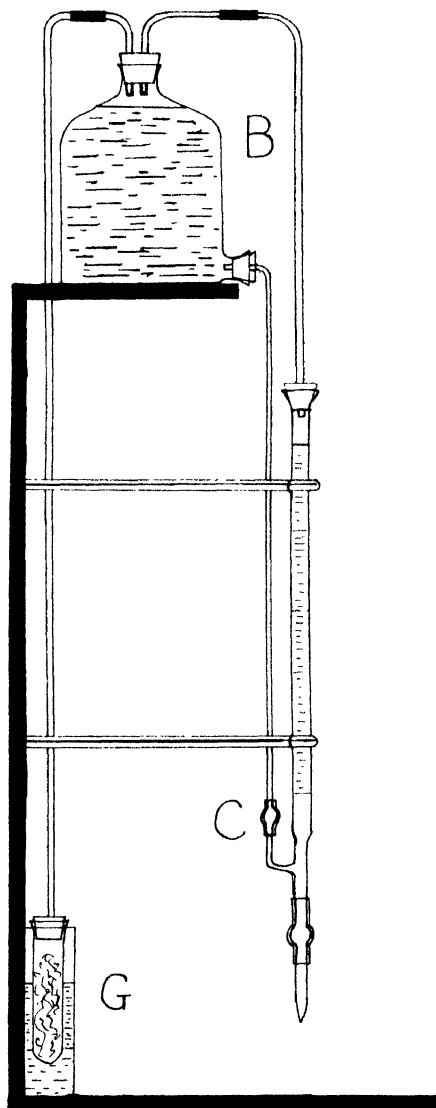
The application of titanous chloride as a quantitative reducing agent [2] has provided a means of valuing a large number of dyestuffs

[1] *J. Soc. Dyers and Col.*, 1885, 1, 74, 201.

[2] Knecht and Hibbert, *New Reduction Methods in Volumetric Analysis*, 2nd ed., London, 1925.

and estimating the percentage of colour taken up by cotton. It is necessary to fit up a special apparatus to protect the reagent from air oxidation, but this is worth the trouble expended because so many substances can be estimated with the solution stored in this way. Up to the present the reagent has not been applied with success to anthraquinone vat colours, auramine and acridine yellow, but there are very few other types to which one or other of the modifications described below is not applicable.

Fig. 131.

The apparatus (Fig. 131) consists of a Wolff's bottle (B) of a little more than 2 litres capacity, fitted at the top with a 2-holed rubber stopper and at the bottom with a stopper having one hole. The top of the bottle is connected to the top of the burette and the bottom of the bottle to the bottom of the burette. The top of the bottle is also connected to a small hydrogen generator (G), placed preferably below the level of the burette exit. A convenient stand with metal supports, which should be well painted, is used to support the apparatus. A tap for the burette consists of a pear-shaped glass bead inside a piece of rubber tubing which is drawn gently to the side with finger and thumb to allow the passage of the liquid. A similar valve is provided at C for filling the burette. Liquid drawn from the burette is replaced by hydrogen which automatically ceases to be supplied when the valve (burette tap) is closed. The bottle is filled with a mixture of 50 to 70 ml. of commercial titanous chloride, 100 ml. of hydrochloric acid and 2 litres

of water. Some considerable variation may be made in the acidity and concentration of the solution. Too much hydrochloric acid leads to inaccurate results in the estimation of nitronaphthalenes and it is best to use only 50 ml. per 50 ml. titanous chloride for such products. Great dilution demands particular care in expelling dissolved oxygen from the water used for diluting the solution, *e.g.* when strengths such as 1 ml. = 0·0002 g. Fe to 0·0005 g. Fe are prepared. The usual strength for dyestuffs (1 ml. = 0·0015 to 0·002 g. Fe) require little or no precautions. The solution is standardized in terms of iron by means of a solution of iron alum of known strength.

Standardization of Titanous Chloride. The best method of standardising the solution is to prepare a solution of pure ferrous ammonium sulphate containing exactly 3·5 g. in 250 ml. dilute sulphuric acid. Oxidize 25 ml. with about *N*/50 potassium permanganate until a faint pink coloration is obtained and then add potassium thiocyanate in excess and titrate with titanous chloride until the red colour is destroyed. If after oxidation 25 ml. iron solution should require 25·4 ml. titanous chloride 0·5 g. Fe and 1 ml. $TiCl_3$ = 0·001968 g. Fe. The thiocyanate is used as internal indicator, but for this purpose it is important to add excess of the reagent. Methylene blue may be used in place of thiocyanate. In doing so only a trace of methylene blue is added or a titration of a known quantity of methylene blue is made separately and another in presence of iron. Iron is completely reduced before methylene blue. Lanterbach [1] has succeeded in rendering the end-point with methylene blue indicator much sharper by adding a little salicylic acid.

In order to avoid frequent weighing and oxidizing it is useful to make an iron alum solution containing 14 g. per litre acidified with sufficient sulphuric acid to give a pale straw-coloured solution instead of the dark brown of the ordinary aqueous solution. A large volume —10 litres—of this may be stored and 25 ml. titrated with the titanous chloride freshly standardized against ferrous ammonium sulphate as described ; afterwards the iron alum solution may be used for any subsequent tests. The iron alum solution is also useful in the indirect method of estimating dyestuffs.

Paranitraniline (m.p. = 149·5°) has been advocated by Callan and Henderson as a reagent for standardizing titanous chloride when that is to be used for estimating nitro-compounds.

For the estimation of particular types of nitro-compounds, Callan and Henderson [2] used titanous sulphate in place of titanous chloride. The authors mix 400 ml. of commercial titanous sulphate with 500 ml.

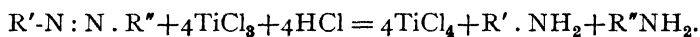
[1] *Ber. d. 7te Internat. Verg. d. Chem.-Kol.*, 1922, p. 35.
[2] *J. Soc. Chem. Ind.*, 1922, 41, 158 T.

of dilute sulphuric acid (1 : 4), boil for a few minutes and make up to 1 litre.

Any reducible substance which can be obtained in a sufficiently pure condition may be used for standardizing titanous chloride or sulphate but, up to the present, the iron standard appears to be most satisfactory and generally adequate.

Titration of Dyestuffs

Method I. Azo-dyes, which are not precipitated by dilute hydrochloric acid, may be titrated directly. This applies to colours like Orange II., Orange G, Scarlet 2G, Crystal scarlet 6R, Scarlet R, Fast red, etc. The azo-group requires four equivalents of titanous chloride, being reduced according to the scheme :—

$$R'\text{-}N:N.R''+4TiCl_3+4HCl=4TiCl_4+R'.NH_2+R''NH_2.$$

For example, 0·5 g. *Crystal scarlet* was dissolved in distilled water and made up to 500 ml. 100 ml. was measured into a conical flask and, after adding 10 ml. of concentrated hydrochloric acid, boiled for about a minute and titrated with titanous chloride, of which 17 ml. was required.

$$1 \text{ ml. } TiCl_3 = 0{\cdot}001712 \text{ g. Fe.}$$
$$502 \text{ g. } C_{20}H_{12}N_2O_7S_2Na_2 = 224 \text{ g. Fe.}$$
$$\therefore \quad \frac{0{\cdot}001712 \times 17{\cdot}1 \times 502}{224} = 0{\cdot}06559 \text{ g. colour}$$

and 1 g. contains :—

0·6559 Crystal scarlet = 65·59 per cent.

This process is applicable to tartrazine. Methylene blue may be estimated by a similar titration, but being converted to a leuco-compound requires only 2 equivalents of titanous chloride. It is best to pass a current of carbon dioxide though the flask during the titration.

Method II. Many of the azo-dyes which are precipitated by hydrochloric acid can be titrated directly in the presence of Rochelle salt or sodium tartrate. A known weight of the dyestuff is dissolved in water, and a definite volume of the solution, together with a solution of sodium tartrate, is titrated with titanous chloride.

The process has been found useful in the valuation of Diamine black, Diamine violet, Benzo green, etc., and it has been used successfully for pure Benzopurpurin and Erika, but commercial samples of these two dyestuffs do not always give distinct end reactions, and the indirect method (III) of titrating azo-dyes is to be preferred for their exact valuation. For example : 1 g. Chlorazol black BH was dissolved

in water and made up to 250 ml. 50 ml. of this solution after addition of 25 ml. Rochelle salt (20 per cent.) required 18·9 ml. $TiCl_3$.

$$1 \text{ c.c. } TiCl_3 = 0{\cdot}001742 \text{ g. Fe}$$
$$960 \text{ g. } C_{54}H_{24}O_{14}N_6S_4Na_4 = 448 \text{ g. Fe.}$$

This solution contains therefore :—

$$\frac{0{\cdot}001742 \times 960 \times 18{\cdot}9 \times 5}{448} = 0{\cdot}3518 \text{ g.}$$
$$= 35{\cdot}18 \text{ per cent.}$$

The method is applicable to certain dyestuffs which yield leuco-compounds and these are best titrated in a flask with carbon dioxide passed over the top of the liquid. Indigotin as disulphonic acid, thioindigo sulphonated, magenta, acid magenta, malachite green, aniline blue (sulphonated triphenyl para-rosaniline), safranine, all require 2H, *i.e.* two equivalents of $TiCl_3$, and for reduction indoine requires 6H.

For Eosine, Rhodamine, Phenolphthalein an addition of alcohol is required in the titration in order to secure a definite end-point; each of these dyestuffs requires 2H.

Although with present-day samples of commercial indigo it is only necessary to sulphonate the indigo, the process has been applied to the valuation of natural indigo.

Bloxam's method depends upon the production and isolation of potassium indigotine tetrasulphonate in the following way :—

1 g. of indigo is sulphonated by heating on a water-bath with 5 ml. of 20 per cent. fuming sulphuric acid for half an hour. The product is then poured into water and made up to 500 ml. 100 ml. is transferred to a large beaker, and 100 ml. of a solution of potassium acetate (450 g. per litre) added. The mixture is boiled, cooled first in a stream of water and then with ice for one hour. Potassium indigotine tetrasulphonate separates out, and this is filtered off through a Gooch crucible. It is then washed with a solution prepared by adding 5 ml. glacial acetic acid to 200 ml. of the potassium acetate solution and 400 ml. water, until the washings lose their brown colour and assume a pale blue tint. The tetrasulphonate is then dissolved in boiling water and, after adding sodium tartrate solution, titrated with titanous chloride in an atmosphere of carbon dioxide.

Titanous chloride decolorizes a solution of Chlorazol sky blue, but on exposure to air or when iron alum is added the colourless solution assumes a red colour. This is characteristic of the colouring matters prepared by combining diazo-compounds with H acid.

It is possible to estimate such colours as Fast acid magenta, Diamine sky blue, etc., by boiling in an atmosphere of carbon dioxide, titrating

with excess of titanous chloride, and then titrating back with iron alum until a faint red colour appears.[1]

A very similar procedure is applicable to Alizarine S (sulphonated alizarine). It is rather curious that 4H are required in this estimation.

Method III. Direct cotton yellows like Chrysophenine cannot be estimated by direct titration. Sodium tartrate yields a compound with titanium which in dilute solution is pale yellow so that the end reaction is obscured if yellow colours are treated according to Method II. An indirect method is therefore used. A known amount of colour solution is boiled in a conical flask into which carbon dioxide is passed. Hydrochloric acid is added, and excess of titanous chloride is run into the mixture. The contents of the flask are again boiled until the colour has been destroyed, which requires about two minutes, and the flask is then cooled in an atmosphere of carbon dioxide which is maintained above the level of the liquid in the flask throughout the estimation. When cold the excess of titanous chloride is titrated with standard iron alum solution using potassium thiocyanate as indicator. By subtracting the number of cubic centimetres of iron alum (or their equivalent in titanous chloride should the two not be of equal strength) from the total number of cubic centimetres titanous chloride run in at first, the exact amount of reducing agent required is arrived at. This is the best way of dealing with direct cotton reds such as Benzopurpurine 4B, nitro-compounds such as picric acid and naphthol yellow S. The direct dyeing azo-colours containing 2 azo-groups require 8 equivalents of titanous chloride and the nitro-compounds require 6 equivalents for each nitro-group.

This process can readily be applied to the estimation of nitro-compounds such as picric acid. Care must be taken, however, to use a large excess of titanous chloride, and to boil for about ten minutes with the reducing agent. By observing these precautions the reduction is complete, six equivalents of titanous chloride being required for the reduction of each nitro-group.

Colouring Matters on Dyed Cotton Fabrics

Estimation of Direct Cotton Colours on the Fibre

The dyed cotton is titrated directly with an excess of titanous chloride, which is afterwards titrated back with iron alum. The process is carried out in a manner similar to the indirect method described for estimation of direct colours in solution.

A weighed quantity of the material is placed in a flask and boiled with dilute hydrochloric acid. Carbon dioxide is then passed

[1] *J. Soc. Dyers and Col.*, 1905, 21, 3.

over, and an excess of titanous chloride is run in. The flask is heated until all the colour has disappeared, when it is cooled, and the excess of titanous chloride is titrated back with iron alum, using potassium thiocyanate as indicator. Generally speaking, 5 g. of cotton is a convenient quantity to use for each estimation, using titanous chloride of the usual strength (1 ml. = 0·0015 to 0·002 g. Fe). Equally good results have been obtained, however, with 1·5 g. cotton and titanous chloride made up so that 1 ml. = about 0·0003 g. Fe.

The method can be employed for direct cotton azo-dyes, and has been proved quantitative in the case of Benzopurpurine 4B, Congo red, Erika, Chrysophenin and Brilliant yellow. For example: 5 g. cotton was dyed with 3 per cent. Benzopurpurine 4B (0·15 g.). The colour was estimated in the bath and on the fibre by the process explained above, being reduced with 50 ml. $TiCl_3$ in each case.

Excess $TiCl_3$ found on fibre, 22·95 ml.
" " " in solution, 23·1 ml. (by iron alum).

1 c.c. $TiCl_3$ = 0·001724 g. Fe = 0·002786 g. benzopurpurine.
(50—22·95) = 27·05 ml. $TiCl_3$ = 0·07536 g. benzopurpurine on fibre.
(50—23·10) = 26·9 ml. $TiCl_3$ = 0·07486 g. benzopurpurine in solution.

Total colour on fibre and in solution = 0·1502 g.

Estimation of Indigo in Dyed Cotton Fabrics

About 4 g. of the dyed cotton is cut up into small pieces and placed in a porcelain beaker; 25 ml. H_2SO_4 80 per cent. strength (148° Tw.) is now added, and the whole is stirred slowly, the temperature being maintained at about 40°. In a very short time the cotton begins to dissolve, and in about ten minutes it has all gone into solution. The contents of the beaker are now diluted with water to about 120 ml. With sulphuric acid of 148° Tw., cellulose is converted into glucose, which remains in solution on diluting with water, while the indigo is converted into a sulphate, which on diluting with water dissociates with the separation of indigotine. This is filtered off through a Gooch crucible containing a filtering medium of quartz and silica. It is best to use as the bottom layer quartz crushed about the size of millet seeds, then a layer of finer quartz about the fineness of grain sugar, and lastly a layer of finely divided silica. The indigo is washed with water, and then sulphonated and titrated in the manner described for pure indigo (see p. 760).

The time required for a complete estimation is a little over two hours.

Colorimetric methods of analysis are described on p. 786 *et seq.*

VIII. FASTNESS TESTS

By J. R. Hannay, F.I.C.

In spite of the large amount of time that has been devoted to this subject for many years, there is still much conflict of opinion as to the best methods for the evaluation of the fastness of the colours of dyed textile materials.

The Colour Index gives a comprehensive scheme of fastness tests, in which a numerical value is attached to the various degrees of resistance shown to the destructive agencies brought to bear on the dyed material. The highest possible degree of fastness is classed as I, whilst the most fugitive colours are rated at V.

The work done by the "Echtheitskommission" of the German Society of Chemists, the labours of the "Fastness Committee" of the American Society of Textile Chemists and Colorists, and the researches and report of the "Fastness Committee" of the Society of Dyers and Colourists in this country, have furnished a basis on which it ought to be possible to found a series of agreed international tests for several types of fastness.

So far the only agreement which has been reached is that fastness should be divided into five grades in which I indicates the lowest and V the highest degree of fastness, except that fastness to light should be divided into 8 degrees, 1 still representing the lowest and 8 the highest degree of fastness.

There are indications that the various committees may be able to agree on standards for some of the measurements in the near future.

The German Fastness Commission has recently published a sixth edition of its report. In order to facilitate the grading, type dyeings have been set up for each test on all the main classes of textile materials. It would be impossible to reproduce here at full length this Commission's report. The report is published by Verlag Chemie G.m.b.H. Berlin W. 36.

1. *Fastness to Light.* The test samples are exposed together with the types, one-half of the samples being covered with opaque paper or cardboard. The exposure is carried out in a glass-covered case, out of doors. The types are dyed on woollen material, with the following dyestuffs :—

	Dyestuff	Amount	
I.	Brilliant Wool Blue FFR extra	0·6 per cent.	
II.	Wool Blue N extra	0·6 ,,	
III.	Brilliant Indocyanine 6B	1·0 ,,	
IV.	Wool Fast Blue GL	1·5 ,,	
V.	Cyananthrol RX	1·3 ,,	
VI.	Alizarine Direct Blue AGG	2·5 ,,	
VII.	Indigosol AZG	2·5 ,,	Decatised.
VIII.	Indigosol Blue AGG	3·0 ,,	,,

2. *Fastness to Water.* The sample is plaited with white scoured cotton yarn, washed zephyr wool and white silk, so that there are two parts of the dyed material to one part of the white materials, and each of the latter is in direct contact with the dyed material. The plait is left overnight in cold distilled water at the ordinary temperature, using a forty times bath, then squeezed and dried at the ordinary temperature.

Standards.	Types.
I. Great change in depth of shade, white strongly stained.	I. Cotton: Cotton Brown A, 2·5 per cent. Wool: Diamond Green GX, 2 per cent. Pure silk: Quinoline Yellow, 0·5 per cent. Weighted silk: Amidonaphthol Red, 5 per cent. Viscose: Rhodamine B extra, 0·5 per cent. Acetate silk: Methylene Blue BGX, 1 per cent. Mordanted.
III. Slight change in depth of shade, white somewhat stained.	III. Cotton: Benzo Red 10 B, 4 per cent. Wool: Fast Red AV, 3 per cent. Pure silk: Acid Violet 4BL, 2 per cent. Weighted silk: Dianil Japonine G, 5 per cent. Viscose: Benzo Brown D3G, 1·5 per cent. Acetate: Celliton Scarlet B powder, 2·5 per cent.
V. Dyeing and white unchanged	V. Cotton: Immedial Carbon B, 8 per cent. Wool: Acid Alizarine Blue Black R. Conc., 3 per cent. Pure silk: Janus Yellow R, 3 per cent. After-treated with tannic acid and tartar emetic. Weighted silk: Janus Yellow R, 2 per cent. Dyed as above. Viscose: Indanthrene Blue GCD fine powder, 3 per cent. Acetate: Cellitazol ST, 3·3 per cent. Developed with Developer ON.

3. *Fastness to Alkalis (Street Mud).* The dyed sample is spotted with a mixture of ammonia 24 per cent. 10 ml., lime 10 g., and water to make 1000 ml. squeezed out, dried at the ordinary temperature without rinsing, and then well brushed.

Standards.	Types.
I. Considerable alteration of shade.	I. Cotton: Chrysamine R., 2 per cent. Wool: Acid Green Conc. S., 2 per cent. Viscose: Phosphine 5R, 1 per cent. Acetate: Rhodamine B extra, 0·5 per cent.
III. Rather considerable alteration of tone of shade.	III. Cotton: Direct Deep Black EW extra, 1 per cent. Wool: Patent Blue V, 2 per cent. Viscose: Direct Deep Black extra 0·5 per cent. Acetate: Cellitazole B, 0·25 per cent, Developed with 1·5 per cent. Developer ON.

Standards.	Types.
V. The tone is unaltered.	V. Cotton: Diamine Black BH, 8 per cent. Developed with meta-toluylene diamine. Wool: Acid Alizarine Blue Black R conc., 3 per cent. Viscose: Indanthrene Blue GCD fine powder, 2 per cent. Acetate: Cellitazole STN, 3·3 per cent. Developed with 4 per cent. Developer ON.

4. *Fastness to Washing.* (*a*) The sample is plaited with an equal weight of cotton and other fibres. The plait is treated in a fifty times liquor containing 5 g. Marseilles soap and 3 g. soda ash per litre at 40° for half an hour. It is then alternately squeezed out in the palm of the hand and dipped again into the bath. Repeat ten times, rinse in cold water and dry.

Standards.	Types.
I. Great change in tone and depth of shade; much bleeding into white.	I. Cotton: Heliotrope BB, 4 per cent. Wool: Diamond Green GX, 2 per cent. Pure silk: Crystal Ponceau 6R, 4 per cent. Weighted silk: Crystal Ponceau 6R, 5 per cent. Viscose: Benzo Brown G, 3 per cent. Acetate: Methylene Blue BGX, 1 per cent. Mordanted.
III. Depth and tone of shade slightly altered. Bleeding none or slight.	III. Cotton: Sirius Fast Blue 3R, 3 per cent. Wool: Milling Red 6BA, 2 per cent. Pure silk: Acid Anthracene Red 3B, 3 per cent. Weighted silk: Benzo Green FFG, 4 per cent. Viscose: Dianil Light Red 12 BW, 2 per cent. Acetate: Cellitone Blue extra powder, 2·25 per cent.
V. Depth and tone unchanged. No bleeding into white.	V. Cotton: Indanthrene Brown R powder, 2·5 per cent. Wool: Acid Alizarine Blue Black R. conc., 3 per cent. Pure silk: Indanthrene Blue GCD fine powder, 10 per cent. Weighted silk: Victoria Blue extra conc., 1 per cent. Aftertreated with tannin and antimony. Viscose: Indanthrene Blue GCD fine powder, 3 per cent. Acetate: Cellitazol STN, 4 per cent. Developed with 4 per cent. Developer ON.

(*b*) The plaited sample is treated in a boiling bath containing 5 g. Marseilles soap and 3 g. soda ash per litre. After half an hour the bath is cooled to 40°, and the sample alternately squeezed out and dipped ten times, as described under (*a*).

Standards.	Types.
I. Great change in tone and depth of shade; much bleeding into white.	I. Cotton: Diamine Orange B, 3 per cent. Pure silk: Fast Red AV, 4 per cent. Viscose: Chrysophenine G, 2 per cent.

Standards.	Types.
III. Depth and tone of shade slightly altered. Bleeding none or slight.	III. Cotton : Immedial Indone Violet B conc., 6 per cent. Pure silk : Algol Scarlet RB, 5 per cent. Viscose : Indanthrene Marine Blue G powder, 3·5 per cent.
V. Depth and tone unchanged. No bleeding into white.	V. Cotton : Indanthrene Brown R powder, 2·5 per cent. Pure silk : Indanthrene Blue GCD fine powder, 10 per cent. Viscose : Indanthrene Blue GCD fine powder, 3 per cent.

5. *Fastness to Stoving.* The sample is plaited with washed Zephyr and white silk. The plait is impregnated in a 0·5 per cent. solution of Marseilles soap at room temperature and squeezed. It is then exposed in a closed vessel to sulphur fumes, obtained from the burning of excess of sulphur, for twelve hours, after which it is well rinsed in cold water, squeezed and dried.

Standards.	Types.
I. Depth and tone of sample altered. White stained.	I. Cotton : Benzo Brown BX, 3 per cent. Wool : Magenta, 2 per cent. Small crystals. Pure silk : Acid Violet BB, 4 per cent. Weighted silk : Acid Violet BB, 4 per cent. Viscose : Orange RO, 3 per cent. Acetate : Methylene Blue BGX, 1 per cent.
III. Depth and tone of sample slightly altered ; white not stained.	III. Cotton : Sirius Light Blue B, 2 per cent. Wool : Acid Violet 4RA, 3 per cent. Pure silk : Alizarine Pure Blue B, 3 per cent. Weighted silk : Acid Anthracene Red G, 3 per cent. Viscose : Diamine Brown 3G, 3 per cent. Acetate : Cellitone Fast Blue R, 8 per cent.
V. Sample unchanged. White not stained.	V. Cotton : Indanthrene Brown powder, 2·5 per cent. Wool : Supramine Brown R, 3 per cent. Pure silk : Indanthrene Blue GCD fine powder, 10 per cent. Weighted silk : Janus Red B, 2 per cent. Aftertreated with tannin and antimony. Viscose : Indanthrene Blue GCD fine powder, 3 per cent. Acetate : Cellitazol STN, 3·3 per cent. Developed with 4 per cent. of Developer ON.

6. *Fastness to Chlorine.* The sample is plaited with an equal weight of cotton, wetted out in hot water and allowed to lie for one hour at room temperature. It is then immersed in sodium hypochlorite solution, containing (*a*) 1 g., or (*b*) 3 g. available chlorine per litre. The solution is made as follows : 100 g. calcium hypochlorite (33 per cent.) is pasted with 400 ml. cold water, and a solution of 60 g. of soda ash in

300 ml. water stirred in for half an hour. After settling, the clear liquor is decanted and mixed with 2 g. soda ash. The clear solution is titrated and made up to the requisite volume. The test is made in a covered beaker.

Standards.	Types.
I. In (*a*) depth and shade much altered. White stained.	I. Cotton: Methylene Blue B, 1 per cent. Viscose: Diamine Brown M, 1·5 per cent. Acetate: Cellitone Blue extra powder, 2·25 per cent.
III. In (*a*) solution, depth and shade little changed. White unstained. In (*b*) solution, shade much altered.	III. Cotton: Algol Brilliant Green BK paste, 20 per cent. Viscose: Hydron Blue R, 1·5 per cent. Acetate: Cellitazol ORB, 3·3 per cent. Developed with 1·5 per cent. phenol.
V. Colour unaltered. White not stained.	V. Cotton: Indanthrene Brown R powder, 2·5 per cent. Viscose: Naphthol AS. TR, 2 g. per litre. Fast Red Base TR, 2 g. per litre. Acetate: Cellitazol B, 0·5 per cent. Developed with 2·5 per cent. Developer ON.

7. *Fastness to Acid.* The dyed material is spotted with (*a*) 10 per cent. sulphuric acid, or (*b*) 30 per cent. acetic acid, and the alteration in shade compared with a spot made with water only.

Standards.	Types.
I. Shade much altered by (*b*).	I. Cotton: Benzopurpurine 4B, 3 per cent. Pure silk: Diamine Brown ATC, 3 per cent. Weighted silk: Diamine Brown ATC, 3 per cent. Viscose: Benzopurpurine 4B, 2 per cent. Acetate: Cellite Fast Yellow R, 1 per cent.
III. Shade much altered by (*a*), but not by (*b*).	III. Cotton: Chrysophenine G, 0·5 per cent. Pure silk: Diamond Green GX, 3 per cent. Weighted silk: Diamond Green GX, 3 per cent. Viscose: Direct Deep Black E, extra, 1·5 per cent. Acetate: Cellitone Red Violet powder, 2·5 per cent.
V. Shade not altered by (*a*).	V. Cotton: Indanthrene Blue RSN powder, 2·5 per cent. Pure silk: Supramine Yellow R, 3 per cent. Weighted silk: Supramine Yellow R, 3 per cent. Viscose: Indanthrene Blue GCD fine powder, 2 per cent. Acetate: Cellitazol STN conc., 3·3 per cent. Developed with 4 per cent. Developer ON.

8. *Fastness to Scrooping.* The sample is immersed at ordinary temperature for five minutes in a thirty times bath, containing 5 g. lactic acid per litre, squeezed and dried without rinsing.

Standards.	Types.
I. Shade much changed.	I. Cotton : Benzopurpurine 4B, 3 per cent. Viscose : Benzopurpurine 4B, 3 per cent. Acetate : Meta Chrome Orange 3R double, 5 per cent.
III. Tone somewhat changed.	III. Cotton : Benzo Olive, 3 per cent. Viscose : Benzo Olive, 3 per cent. Acetate : Cellite Fast Red BB, 3 per cent.
V. No change.	V. Cotton : Indanthrene Blue RSN powder, 2·5 per cent. Viscose : Indanthrene Blue GCD fine powder, 3 per cent. Acetate : Cellitazol STN conc., 3·3 per cent. Developed with 4 per cent. Developer ON.

9. *Fastness to Cross Dyeing.* The dyed sample is plaited with an equal weight of wool and white cotton. It is then boiled for one hour in a forty times bath of 10 per cent. sodium bisulphate on the weight of material, rinsed in cold water, squeezed and dried.

Standards.	Types.
I. Depth and tone of shade altered ; white wool stained.	I. Cotton : Magenta crystals, 1 per cent. Wool : Patent Blue V, 2 per cent. Viscose : Rhodamine B Extra, 1 per cent. Acetate : Cellite Fast Blue STN conc., 3·3 per cent. Developed with 4 per cent. Developer ON.
III. Depth and tone little changed or unchanged, wool slightly stained.	III. Cotton : Zambesi Red B, 2 per cent. Developed with β-naphthol. Wool : Supranol Scarlet G, 2 per cent. Viscose : Diazo Brown 3R, 3 per cent. Developed with β-naphthol. Acetate : Cellitazol SR, 1 per cent. Developed with resorcin.
V. Shade unaltered. White wool unstained.	V. Cotton : Indanthrene Blue fine powder, 4 per cent. Wool : Indigosol Brown IRRD, 5 per cent. Viscose : Indanthrene Blue GCD fine powder, 3 per cent. Acetate : Cellitazol STN conc., 3·3 per cent. Developed with 4 per cent. Developer ON.

10. *Fastness to Ironing.* The dyed material is covered with a double strip of thin, white, pure cotton cloth, and ironed with an iron just hot enough to scorch white woollen felt. Ironing is continued till the strips are quite dry. Acetate silk is treated with an iron between 96° and 104°. A crystal of α-naphthol should melt on the iron, but pyrocatechol must remain unmelted (m.p. 110°).

Standards.	Types.
I. Depth and tone much changed. The original shade returns after some considerable time.	I. Cotton: Brilliant Benzo Violet B, 1 per cent. Wool: Acid Magenta O, 2 per cent. Pure silk: Acid Magenta O, 4 per cent. Weighted silk: Acid Magenta O, 6 per cent. Viscose: Benzo Rhoduline Red B, 6·5 per cent. Acetate: Cellite Fast Blue A, 3 per cent.
III. Depth and tone little changed. On cooling, shade returns quickly.	III. Cotton: Benzopurpurine 4B, 1 per cent. Wool: Victoria Rubine O, 2 per cent. Pure silk: Naphthylamine Brown, 5 per cent. Weighted silk: Supranol Brilliant Red 3B, 4 per cent. Viscose: Benzo Fast Scarlet 6BSS, 3 per cent. Acetate: Cellitone Red powder, 5 per cent.
V. Shade unchanged. White not stained.	V. Cotton: Indanthrene Green BB powder, 1·25 per cent. Wool: Tartrazin, 2 per cent. Pure silk: Indanthrene Blue GCD fine powder, 5 per cent. Weighted silk: Coerulein S, 3 per cent. Viscose: Indanthrene Blue GCD fine powder, 2 per cent. Acetate: Cellitazol STN conc., 3·3 per cent. Developed with 4 per cent. Developer ON.

11. *Fastness to Rubbing.* The dyed material is rubbed ten times over a distance of 10 cm. backwards and forwards with a strip of white pure cotton cloth stretched over the forefinger.

Standards.	Types
I. The dyeing rubs badly.	I. Cotton: Diamond Green BXX, 2 per cent. Wool: Diamond Green GX, 2 per cent. Pure silk: Diamond Green GX, 8 per cent. Weighted silk: Diamond Green GX, 6 per cent. Viscose: Rhodamine B extra, 1·5 per cent. Acetate: Methyl Violet B extra conc., 0·5 per cent. Dyed on mordanted material.
III. The colour rubs slightly.	III. Cotton: Primuline, 0·4 per cent. Developed with β-naphthol. Wool: Patent Blue A, 2 per cent. Pure silk: Azoflavine 3G extra special, 5 per cent. Weighted silk: Azoflavine 3G extra special, 4 per cent. Viscose: Primuline O, 5 per cent. Developed with β-naphthol. Acetate: Cellit Fast Violet, 3 per cent.

Standards.	Types.
V. The colour does not rub.	V. Cotton: Naphthogen Blue RR, 3 per cent. Developed with β-naphthol. Wool: Alizarine Rubinol R., 2 per cent. Pure silk: Amido Yellow E, 2 per cent. Weighted silk: Amido Yellow E, 3·5 per cent. Viscose: Chrysophenine G, 2 per cent. Acetate: Cellitazol B, 0·25 per cent. Developed with 1·5 per cent. Developer ON.

12. *Fastness to Perspiration.* The dyed material is plaited with cotton and wool. When testing acetate silk, strands of pure silk and acetate silk are plaited in as well. The plait is immersed in a ten times bath at 45°, containing 5 g. salt and 6 ml. ammonia (24 per cent.) per litre. During half an hour, squeeze out by hand ten times, every ten minutes. Then add 7·5 ml. glacial acetic acid per litre and again squeeze ten times every ten minutes for half an hour. Squeeze and dry without rinsing at the ordinary temperature.

Standards.	Types.
I. Depth and tone of shade change greatly. Much bleeding into white.	I. Cotton: Brilliant Sky Blue 8G extra, 4 per cent. Wool: Azogranadine S, 2 per cent. Pure silk: Victoria Rubine O, 4 per cent. Weighted silk: Victoria Rubine O, 4 per cent. Viscose: Brilliant Sky Blue 8G extra, 4 per cent. Acetate: Methylene Blue BGX, 1 per cent. On mordanted material.
III. Depth and tone little changed, or not at all. White somewhat stained.	III. Cotton: Benzoform Red GGF, 2 per cent. Aftertreated with 2 per cent. formalin. Wool: Brilliant Milling Red B, 2 per cent. Pure silk: Diazo Brilliant Scarlet BBL extra, 5 per cent. Developed with 1·5 per cent. β-naphthol. Weighted silk: Diazo Brilliant Scarlet 6B extra, 4 per cent. Developed with β-naphthol. Viscose: Diamine Fast Red F, 3 per cent. Aftertreated with chromium fluoride. Acetate: Cellitone Fast Blue BF powder conc., 2·5 per cent.
V. No change in shade. White not stained.	V. Cotton: Indanthrene Brown R powder, 2·5 per cent. Wool: Diamond Black PV, 8 per cent. Pure silk: Indanthrene Blue GCD fine powder, 5 per cent. Weighted silk: Janus Red B, 2 per cent. Aftertreated with tannin and antimony. Viscose: Indanthrene Blue GCD fine powder, 2 per cent. Acetate: Cellitazol SR, 1 per cent. Developed with 1·5 per cent. phenol.

13. *Fastness to Sea Water* (*Wool only*). The dyed sample is plaited with white wool and steeped for twenty-four hours in a forty times bath containing 30 g. salt and 6 g. calcium chloride (anhydrous) per litre. It is then squeezed and dried without rinsing.

Standards.	Types.
I. Depth and shade little altered, but white wool badly stained.	I. Azo Grenadine S, 2 per cent.
III. Colour altered slightly or not at all. White considerably stained.	III. Patent Blue A, 1 per cent.
V. Colour not altered. White not stained.	V. Diamond Black PBB, 5 per cent.

13. *Fastness to Potting.* The dyed sample is plaited with equal weights of wool and cotton. It is then steeped for two hours in a seventy times bath of distilled water at 90°, rinsed and dried.

Standards.	Types.
I. Colour much affected. White badly stained.	I. Wool: Patent Blue A, 2 per cent. Viscose: Chrysophenine G, 2 per cent. Acetate: Cellite Fast Orange G, 1 per cent.
III. Shade not or hardly affected. White strongly stained.	III. Wool: Diamond Black F, 5 per cent. Viscose: Diazo Indigo Blue 3RL, 2 per cent. Developed with β-naphthol. Acetate: Cellitazol RB, 0·75 per cent. Developed with 1·5 per cent. phenol.
V. Colour hardly affected or not at all. White less stained than in I.	V. Wool: Diamond Black PV, 1 per cent. Viscose: Indanthrene Blue GCD fine powder, 3 per cent. Acetate: Cellitazol B, 0·25 per cent. Developed with 1·5 per cent. Developer ON.

14. *Fastness to Milling.* (*a*) Neutral Milling. The sample is plaited with equal weights of wool and cotton. It is then immersed in a forty times bath containing 20 g. Marseilles soap per litre at 30°. It is well rubbed and squeezed in the hands, allowed to lie in the liquor for two hours, milled again, well washed and dried.

(*b*) Alkaline Milling. The plait is milled in a solution containing 50 g. Marseilles soap and 5 g. soda ash per litre at 40°, at intervals of fifteen minutes for two and a half hours. Then rinsed and dried. Wool, silk and viscose are treated in both neutral and alkaline liquors. Acetate silk in the neutral bath only.

Standards.	Types.
I. Milled neutral. Depth and tone much altered. White badly stained.	I. Wool: Orange II, 2 per cent. Pure silk: Fast Red AV, 4 per cent. Viscose: Rhodamine B extra, 1 per cent. Acetate: Methylene Blue BGX, 1 per cent. On mordanted material.
III. Milled neutral. Colour unaltered; white not stained. Milled alkaline. Depth and tone much altered. White stained.	III. Wool: Sulphoncyanine Black BB, 6 per cent. Pure silk: Janus Yellow G, 2 per cent. Viscose: Diazo Brown 3R, 4 per cent. Developed with β-naphthol. Acetate: Celliton Blue extra powder, 2·25 per cent.

Standards.	Types.
V. Milled alkaline. No change in shade. White not stained.	V. Wool: Diamond Black PBB, 5 per cent. Pure silk: Indanthrene Blue GCD fine powder, 10 per cent. Viscose: Indanthrene Blue GCD fine powder, 3 per cent. Acetate: Cellitazol STN, 3·3 per cent. Developed with 4 per cent. Developer ON.

15. *Fastness to Hydrogen Peroxide Bleach.* Plait the dyed material with white wool, cotton and silk yarn, and steep in a forty times bath containing 100 ml. water, and 20 ml. 10-volume hydrogen peroxide, made alkaline with ammonia to *p*H 10. Warm to 50° and leave for twelve hours, rinse and dry.

Standards.	Types.
I. Shade and depth not, or little, altered. Wool, silk and cotton are stained.	I. Wool: Metanil Yellow extra, 2 per cent. Pure silk. Fast Red AV, 4 per cent. Viscose: Rhodamine B extra, 1 per cent. Acetate: Methylene Blue BGX, 1 per cent. On mordanted material.
III. Depth and shade altered. Wool, silk and cotton slight, or not at all, stained.	III. Wool: Patent Blue A, 3 per cent. Pure silk: Acid Anthracene Brown KE, 8 per cent. Aftertreated with 1·5 per cent. sodium bichromate. Viscose: Benzo Red 10B, 3 per cent. Acetate: Cellitone Red Violet R powder, 2·5 per cent.
V. Shade altered very slightly, or not at all. Whites not, or slightly, changed.	V. Wool: Indigosol O, 10 per cent. Pure silk: Indanthrene Blue GCD fine powder, 10 per cent. Viscose: Indanthrene Blue GCD fine powder, 3 per cent. Acetate: Cellitazol STN conc., 3·3 per cent. Developed with 4 per cent. Developer ON.

16. *Fastness to Carbonizing.* The sample is steeped in $7 \cdot 5^\circ$ Tw. sulphuric acid for half an hour, squeezed to contain 100 per cent. of liquor, and dried at 80° for one hour. It is then washed with 200 times its weight of water, squeezed, neutralized in 0·2 per cent. soda ash solution for fifteen minutes, followed by thorough washing till neutral to litmus paper. This test is applied only to dyed wool.

Standards.	Types.
I. Depth and shade changed considerably.	I. Alizarine W powder, 2 per cent.
III. Depth and shade changed slightly.	III. Amidonaphthol Red G, 2 per cent.
V. Change of colour slight or none.	V. Palatine Scarlet A, 2 per cent.

17. *Fastness to Decatizing.* Six layers of dry steaming cloth are wound on to the steaming cylinder, then the dyed sample is wound on evenly, followed by three

more layers of steaming cloth. The whole is then tied up. This test is applied to wool and viscose only.

(*a*) Steam is blown through at half an atmosphere pressure for ten minutes.

(*b*) Steam is blown through for ten minutes at 1½ atm. pressure.

Standards.	Types.
I. Depth and shade much altered at ½ atm.	I. Wool: Thioflavin T, 2 per cent. Viscose: Sulphoncyanine G, 3 per cent.
III. At ½ atm. no change. At 1½ atm. shade and depth much changed.	III. Wool: Sulphoncyanine GR extra, 2 per cent. Viscose: Diamine Fast Violet BBN, 3 per cent.
V. No change at 1½ atm.	V. Wool: Naphthol Blue Black S, 6 per cent. Viscose: Indanthrene Blue GCD fine powder, 2 per cent.

18. *Fastness to Soda Ash Boil.* The sample is plaited with an equal weight of grey cotton yarn and boiled for one hour in a twenty times liquor containing 10 g. soda ash per litre. The volume is kept constant by the addition of more water. The test is applied to cotton only.

Standards.	Types.
I. Depth and shade much altered. White deeply stained.	I. Benzopurpurine 4B, 4 per cent.
III. Depth and tone somewhat altered. White stained.	III. Algol Violet R powder, 1·5 per cent.
V. Dyeing and white cotton unchanged.	V. Indanthrene Khaki GG powder, 2·5 per cent.

19. *Fastness to Caustic Soda Boil.* (*a*) The dyed material, plaited with an equal weight of bleached cotton yarn, is boiled for six hours in a ten times bath containing 10 per cent. of 76° Tw. caustic soda solution, calculated on the weight of material, keeping the volume of liquor constant by the addition of more water. Rinse well, squeeze and dry.

(*b*) Carry out the boil as above, but with the addition of 1 per cent. of Ludigol on the weight of material. These tests are used for dyed cotton only.

Standards.	Types.
I. Depth and shade much altered both in (*a*) and (*b*) liquors. White cotton considerably stained.	I. Paranitraniline Red.
III. Depth and shade distinctly changed both in (*a*) and (*b*). White cotton little, or not at all, stained.	III. Cotton prepared in Naphthol AS.TR, 4 g. per litre. Developed with 2 g. Fast Red Base TR per litre.
V. Shade unaltered in both (*a*) and (*b*). White cotton shows little or no staining.	V. Cotton prepared in 3 g. Naphthol AS.G and 15 g. salt per litre. Developed with 1·65 g. Fast Yellow Base GC per litre.

20. *Fastness to Mercerizing.* Plait the dyed sample with bleached, pure cotton and steep for two minutes in cold 52° Tw. caustic soda solution containing 10 ml.

Prestabit Oil BMD per litre as wetting out agent. Wash off, sour, wash free from acid and dry. This test only applies to cotton.

Standards.	Types.
I. Colour and depth much altered. White stained.	I. Isamine Blue 6B, 3 per cent.
III. Depth and tone slightly changed. White slightly stained.	III. Dianil Orange 6B, 3 per cent.
V. Shade unaltered. White unstained.	V. Indanthrene Brown R powder, 2·5 per cent.

21. *Fastness to Sodium Peroxide Bleach.* (*a*) Plait together 2 g. dyed sample and 2 g. white cotton, and steep overnight in 100 ml. diastofor solution containing 1 g. per litre at 60°. Wash and immerse in 200 ml. of a solution containing 3 g. per litre of sodium peroxide. Warm within three-quarters of an hour to 90° and maintain at this temperature for a further three-quarters of an hour. Rinse, sour, rinse and dry.

(*b*) Treat with diastofor as above, then steep in cold bleaching liquor containing 1 g. active chlorine per litre. Rinse, sour, wash off and enter into peroxide solution as above. These tests are for cotton only.

Standards.	Types.
I. In process (*a*) shade much weakened, and white badly stained.	I. Immedial Green GG extra, 15 per cent.
III. After process (*a*) some loss in depth and change of shade. White somewhat stained. By procees (*b*) great change in shade and white stained.	III. Algol Scarlet GG powder, 5·4 per cent.
V. After process (*b*) no change in shade and white unstained.	V. Indanthrene Gold Orange 3G powder, 1 per cent.

The report of the Fastness Committee of the Society of Dyers and Colourists published in 1934 deals with three types of fastness only, viz.: Fastness to Light, Fastness to Perspiration, and Fastness to Washing.

For measuring fastness to light the committee recommend a set of seven red and seven blue standards numbered II to VIII, dyed on a specified quality of woollen serge. As accurate reproduction of carefully standardized conditions of dyeing is essential if any degree of comparability is to be looked for in the tests made at different times and by different operators, the committee does not give detailed instruction for dyeing the standards, but the Society supplies quantities of the standard patterns at a fixed charge. The standards have been selected because they fade in the same ratio to one another under a fairly wide range of exposure conditions, and the classification of

samples tested against them is approximately the same whether the illumination is sunlight or electric arc.

After reviewing recent work on the composition of human sweat, the committee prescribe two test solutions for fastness to perspiration, one being slightly alkaline, *p*H 7·8, and the other slightly acid, *p*H 5·6. The dyed pattern along with undyed cotton and wool is saturated with the reagent, lightly squeezed, and then incubated at a temperature of 37° for four hours. There is no grading. The sample either does or does not stand perspiration.

In the recommended tests for fastness to washing, an attempt is made to overcome the variable factor introduced by hand-washing methods, by the use of a specially constructed wash wheel. As in the light fastness test, a set of five red and five blue standards dyed on a specified plain cotton limbric is recommended. These are to be obtained from the Society. Four tests of increasing severity are prescribed, and cover all types of textile scouring, from a mild home wash to a test representing the cumulative action of several severe power washes.

The report and the standards may be obtained from The Society of Dyers and Colourists, 32-34 Piccadilly, Bradford, Yorks.

A committee of the Paper Makers' Association of Great Britain and Ireland appointed to recommend a Standard Method of Determining the Fastness to Light of Coloured Paper published a very interesting interim report in October 1936.

Although this naturally deals with the problem from the paper-maker's standpoint, it contains many observations and criticisms of accepted methods which are valuable to all interested in the problem of standardizing light-fastness tests. In particular, attention is drawn to the great difficulty in obtaining similar judgments on one set of tests from different observers. Thus when a series of 45 samples were submitted to scrutiny by 36 observers, only 29 per cent. of the samples were placed similarly by all the observers, when ordinary visual examination was used. By using a specially constructed viewing box this was raised to 42 per cent. on a first judgment, and 76 per cent. on a second judgment. This indicates the advantage to be gained from the use of a special apparatus, but leaves a doubt whether any method of visual observation can ever be satisfactory.

There are instruments which will give a scientific analysis of the colour of the sample both before and after fading, but such instruments are exceedingly costly and require very skilled operation to obtain results of any value. While the careful application of recognized methods of testing will give results which may be of considerable technical and commercial value, the establishment of reliable universal standards has not yet been attained.

IX. COLORIMETRY AND SPECTROPHOTOMETRY[1]

By R. Guelke, Ph.D.

A. The Basis of Colorimetry

The term colorimetry is applied in a rather loose sense both to spectrophotometry in the visual region and to the measurement of the psychological effect of light of a given quality on the eye, *i.e.* the measurement of " colour " in the strict sense of the word. Colorimeters and spectrophotometers are of two types. Some are constructed to identify and measure the quantities of any substance present. The justification for calling some of these instruments colorimeters is that their use depends on certain properties of the eye, in particular on the capability of the eye for detecting differences in colour. The eye is, so to speak, a very sensitive nullpoint instrument, and is in some cases replaced by a photocell. Others, true colorimeters, are constructed for the purpose of specifying a colour and describing as accurately as possible how that colour would appear to a normal eye (*e.g.* the Guild trichromatic colorimeter). Thus, in the first case, the optical properties of substances are used to determine the quantities of those substances present, whereas in the second case the properties of the substances as judged by the eye are determined. As the appearance of a substance to the eye is determined by its physical properties in relation to radiation and this relation has been determined, it is possible to calculate the appearance from a thorough investigation of the purely physical characteristics of a substance. On the other hand, it is not possible to compute the physical characteristics from the appearance as determined by a trichromatic match. It is therefore apparent that for general purposes the methods for determining the physical properties will be more important.

The properties of a substance in relation to radiation depend upon the transmission and the reflection of radiation. Without investigating the details of the laws governing the reflection of light exactly, it is sufficient to note that the amount reflected depends upon the angle of incidence and the refractive index. In most cases this latter is independent of the absorption. The absorption only becomes effective when it is appreciable at a distance of one wavelength from the surface—for instance, in metals or solid dyestuffs showing a " metallic " lustre. The " texture " of a substance is usually determined by the reflection and the number and shape of the reflecting surfaces (see lustre, etc.), whereas the colour of a substance is nearly

[1] For more detailed information see: Baly, *Spectroscopy*, London, 1924-27; Kayser, *Handbuch der Spektroskopie*, Leipzig, 1900-12; Lifschitz, *Spectroskopie und Colorimetrie*. Leipzig, 1927; Weigert, *Optische Methoden der Chemie*, Leipzig, 1927.

always determined by the relative absorption of light passing through a substance and being subsequently reflected out again. Thus differences in appearance, in particular in the case of textiles, will be due to differences in the transmission of light of different wavelengths. A treatment of the problem of calculating the light reflected from a textile surface from the transmission of the individual fibre is given by various authors.[1] In spite of the fact that it is much more usual to look at anything rather than to look through it, the measurement of the transmission of solids and liquids is of greater interest and much easier to accomplish owing to the simplicity of the laws involved. The degree of accuracy is higher and the conditions far less critical than for reflected light.

To describe the transmission of a substance, it is necessary to have a measure of the amount of light passed by that substance at each wavelength over the range which it is desired to investigate. This measure is chosen so that a higher number means a higher opacity and zero, complete transparency. It is known as the " density " and is defined by the following equation :—

$$D = \log_{10}\frac{Io}{I} \qquad (1)$$

where D = density,
Io = intensity of light before passing through the substance.
I = intensity of light after passing through the substance.

The great advantage of defining the density in this manner is that the densities of a number of filters [2] are additive. Thus, if one filter has the density D_1 at a wavelength λ, another D_2 at the same wavelength, then the two filters superimposed will have the density D_1+D_2 at wavelength λ.

If the optical density of a filter is determined for each wavelength over a range, a curve can be drawn representing the optical density as a function of the wavelength. This is known as the " absorption curve " of the filter. The absorption curve of a solid substance is defined as the absorption curve of a filter with a thickness of 1 cm.

Since density is additive, the optical density of a substance is directly proportional to the thickness, and it is possible to calculate the density at any thickness if the density at one thickness is known (Lambert's law). Of much greater interest than the optical density of solids is the density of solutions. Dyed fabrics can generally be regarded as solutions of the dyestuff in cotton. Whereas it is inconvenient to prepare thin sheets of a solid for examination by transmitted light (and sheets of colouring matters would have to be

[1] Guelke and Fitzsimons, *Trans. Farad. Soc.*, 1934, **30**, 512 ; Tsien, *M.Sc. Tech. Thesis*, Victoria University, Manchester, April 1937.

[2] The term " filter " here means a layer of a transparent light-absorbing material.

extremely thin as the density would otherwise be so high as not to be measurable by ordinary methods), it is easy to dissolve them in some colourless solvent and dilute it down until a solution of suitable optical density is obtained. If a suitable solvent is found and dilute solutions are used, the density is directly proportional to the concentration (Beer's law). Combining this with Lambert's law the following equation is obtained :—

$$D = \alpha ct \qquad (2)$$

where α is the extinction coefficient,
c is the concentration,
and t the thickness.

This is the most important relationship in colorimetry, and from it a number of important conclusions can be derived. Thus two dilute solutions of a substance will appear the same if viewed in thicknesses inversely proportional to their concentration. Because α is the same in both cases for all wavelengths (same substance), D is also the same for any wavelength (same appearance). Therefore :—

$$c_1 t_1 = c_2 t_2 \qquad (3)$$

This relationship is used in a number of colorimeters such as the Dubosc, Nessler tubes, etc.

The equations (1), (2) and (3) are applicable only to monochromatic light. It is therefore necessary not only to measure the extinction coefficient α at one wavelength, but to do so for the whole range of wavelengths for which it is desired to characterize the substance. Some sort of photometer head must be employed for measuring the density, and also some source of monochromatic light is required to enable the density measurement to be made at definite wavelengths over a range. Instruments for measuring the density over a range of wavelengths are known as spectrophotometers. They are described below.

B. Instruments

(*a*) Methods of obtaining Monochromatic Light

Spectrometers. The usual method of obtaining monochromatic light is to use a prism spectroscope or spectrograph. A great variety of these instruments is on the market, varying widely in dispersion, aperture, and range. For colorimetric work it is usually necessary to employ an instrument capable of delivering a considerable light intensity. It is therefore usual to use a prism instrument because the amount of light available is greater than from the grating instruments.

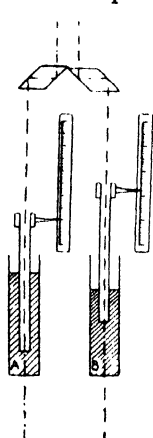
A spectrometer without any further attachment can conveniently be used to determine the absorption maxima of solutions. Formanek uses this method for the identification of dyestuffs, and for this purpose it

can be useful provided one colouring matter only is present. As, however, this condition is seldom fulfilled in practical work, the results are only of limited value. It may be mentioned in this connection that all prism spectrometers show an intensity maximum in the yellow when used with the usual light sources. If it is desired to judge the position of the absorption maxima more accurately, it is often useful to place in the optical path a cell containing methylene blue solution of sufficient concentration to render the appearance of the spectrum more even.

When using monochromators particular attention should be paid to the fact that most instruments do not give pure monochromatic light, but monochromatic light plus a considerable amount of stray light of all wavelengths due to internal reflections, etc. Therefore, if work of the highest accuracy is required, it is advisable to use a double monochromator or, if that is not available, to use a filter (combined with the monochromator) to absorb most of the unwanted light.

Most dyestuffs have fairly broad absorption maxima ; for a number of purposes it is therefore sufficient to use a filter transmitting a narrow band of the spectrum instead of a monochromator. This has several advantages. There is much less stray light outside the band if a filter is used than with a single monochromator. The available intensity is much greater and the whole surface of the light source can be used. If the aim is to determine the amount of dyestuff present in a solution, monochromatic filters are as good, if not better, than a prism monochromator.

(*b*) Methods of Comparison

Having obtained monochromatic light, the next problem is to measure the actual extinction coefficient of the substance at the wavelength chosen. This can be achieved in a number of different ways, the choice of which depends mainly on the region to which the wavelength belongs, and the result which is required. If it is only necessary to compare two solutions of the same substance to determine their relative concentrations, it may even be possible entirely to dispense with a source of monochromatic light. By adjusting either the thickness or the concentration of one sample until both appear equal, it is possible to calculate the concentration ratio as the inverse ratio of the thicknesses, or if the concentration has been adjusted, the ratio can be calculated directly.

If the concentrations are adjusted, no special apparatus is required (beyond the normal apparatus employed in volumetric analysis). This method is, however, not recommended because of the difficulty

of continuous adjustment. Once a solution is diluted too much it is not easy to correct the error.

If a simple method of comparison is required which does not involve the use of expensive apparatus, Nessler tubes can be employed. These are really nothing but measuring cylinders with a flat bottom. They are used by adjusting the height until a piece of white paper placed underneath appears the same colour in both tubes. The inverse ratio of the height is then the ratio of the concentrations.

These primitive methods suffer from the disadvantage that the comparison is made between two fields that are not touching, and continuous adjustment cannot be made merely by turning a knob. For greater accuracy and rapidity a colorimeter of the Dubosc type is therefore of great assistance because it embodies both these features.

The principle of the Dubosc colorimeter is illustrated in Fig. 132.

Fig. 132.

Two parallel beams of light of equal intensity are passed through the liquids contained in two similar beakers. The thickness of liquid through which the beam has to pass is regulated by a plunger which can be moved up or down. A scale then measures the thickness of the liquid under observation. The two beams emerging from the liquids through the plungers are then passed through a prism which is designed to throw both beams close to each other in the field of view. This is usually so arranged that one semicircle of the field is illuminated by one and the other semicircle by the other beam. It is then possible to focus the dividing line sharply. By adjusting the plungers this line can be made to disappear if two solutions of the same substance are viewed, and the inverse ratio of the thicknesses is equal to the ratio of the concentrations as before.

It often happens that the greatest accuracy cannot be obtained from a Dubosc because the solutions which it is desired to measure are not exactly the same colour. This is usually due to the presence of coloured impurities which can, of course, render any colorimetric determination impossible if they are present to any great extent. These impurities often only cause a slight difference in shade, which, although it does not render the colorimetric determination impossible, makes it difficult to adjust the fields to equality. In that case the use of a monochromatic filter will often make the results much more accurate.

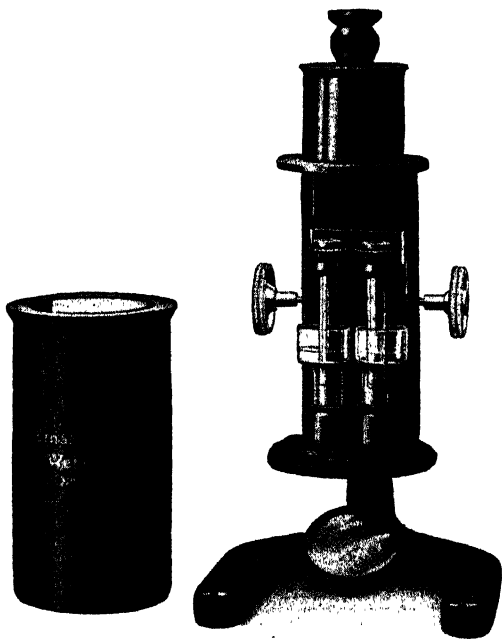
A large number of models of Dubosc colorimeters are available. The following are some points which should be considered when choosing such an instrument:—

1. The two paths of light should be entirely independent of each other. If an opaque object is placed in the path of one beam, the corresponding field should not show any stray light.
2. Suitable covers should be available for excluding the light from outside.
3. The movement of the plungers should be smooth and easily adjustable. The scale should be well illuminated and preferably equipped with a vernier.
4. The beakers and plungers should preferably be so constructed that no cement is used. Considerable trouble is avoided if no liquid need be banned because of its action on the beakers or rods. It is sometimes desirable to use concentrated sulphuric acid as a solvent.

Fig. 133 shows a simple Dubosc, and Fig. 134 shows a three-stage instrument as used for *p*H determinations. A special grey solution is supplied with this instrument which obviates the necessity for a fresh standard for each substance under investigation.[1] A series of eleven spectral filters are mounted in the eye-piece for use with the grey solution.

FIG. 133.

For certain measurements, two-stage or even three-stage instruments have some advantages. If, for example, coloured substances are present other than the one it is desired to estimate they are usually allowed for by measuring a " blank " first, on a solution of these substances alone. With a two-stage instrument this can be done automatically by placing the solution of the substances that are interfering with the correct measurement in the path of the light which is used as the standard of comparison.

This method of compensation can be used only if the two substances do not interfere with each other in solution. This can easily be checked on a two-stage instrument by comparing the field produced

[1] " The Absolute Colorimeter," Guelke, *J. Soc. Dyers and Col.*, 1934, **50**, 77.

by the combined effect of each solution separately on the one hand and of a mixture of the two solutions on the other. If the thicknesses of the individual solutions are chosen proportional to their relative concentration in the mixture, and the thickness of the mixture is chosen to equal the sum of the thicknesses of the two individual

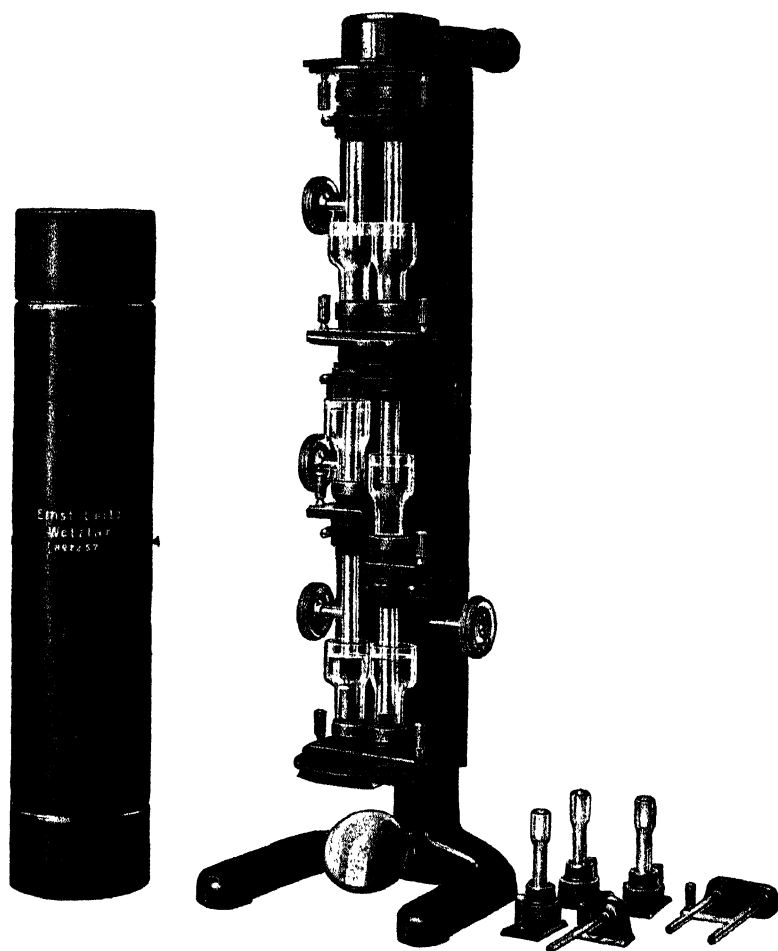



FIG. 134.

solutions, then the fields should be a match. This follows directly from an extension of Beer's law to mixtures.

Where the rapid estimation of concentrations of solutions is required, the Dubosc colorimeter is the ideal instrument to use, but for the accurate determinations of the absorption curve of a solution it suffers from the disadvantage that it cannot easily be adapted for use with a monochromator. For determining concentrations, the fact

that strictly monochromatic light is not available will seldom be of great moment, and as the field in a Dubosc is usually fairly large, the accuracy and reproducibility of the measurements will often be better than those obtained with spectrophotometers using a monochromator. For showing small changes in the position of the absorption maxima, and at the same time measuring alterations in the height of the absorption peak, a spectrophotometer of some sort is necessary.

The essential requirements of a spectrophotometer are (*a*) a source of monochromatic light, (*b*) a means of measuring the extinction coefficient. The former has been dealt with above.

(c) Methods of measuring the Absorption Coefficient

These methods can be roughly divided into visual methods, photo-electric methods, and photographic methods.

Visual Methods. The principle of all visual methods is to divide the light into two beams of equal intensity (or intensities having a fixed ratio). The solution (or substance) which is being measured is then placed in the one beam and the intensity of the other beam is then cut down until the two beams are of equal intensity as judged by the eye. The two beams are brought into juxtaposition as described above for the Dubosc. The amount by which the second beam has to be cut down in intensity is then a quantitative measure of the amount by which the light of the first beam is weakened on passing through the sample. The amount by which the light is cut down has to be measured, therefore some method of doing this must be used which is continuous and also permits of measurement. A method which enables this to be done so that the result is easily measured is to use two polarizing prisms and to measure the angle between them. The intensity is then proportional to $\text{Cos}^2\,\theta$ when θ is the angle between the axes of the two prisms. In some instruments the two beams are both made to pass through polarizing prisms with their axes perpendicular to each other, and when they are brought together again for observation they are passed through another polarizing prism. The intensity expressed as a function of the position of this third prism is then proportional to $\tan^2\,\theta$. An example of this type of instrument is the Hilger-Nutting photometer.

Instead of using two polarizing prisms to cut down the light, a diaphragm or a wedge can be used. An instrument using a diaphragm is the Zeiss step photometer. Diaphragms have to be very well made and the light path has to be well designed if they are to be accurate, but they have the advantage that they are independent of wavelength.

Density wedges are used in some instruments, and although some wedges are neutral and permanent, others have been known to fade,

and many are liable to be less dense in the red than in other parts of the spectrum.

All the above instruments rely on the eye to judge when two fields are equal. They have the advantage of being comparatively simple in construction and, if well designed, they are not likely to go out of adjustment. When using these instruments it is always advisable to take several readings, both of the " blank " and of the " sample." It should then be possible to obtain an accuracy to 0·01 in density, *i.e.* 2 to 3 per cent. in intensity. An untrained observer is not likely to attain this degree of accuracy, so that for general work 5 per cent. in intensity can be considered fairly good. But the eye is not only limited in accuracy, it is also confined to the comparatively narrow region of the spectrum between 7000 Å and 4000 Å. Other methods are used with a view to increasing both range and accuracy.

Photo-electric cells are most commonly used if greater accuracy is required. The equipment necessary to realize this higher degree of accuracy is neither simple nor easy to use. Although several individual instruments are in use for this purpose, there is as yet no simple photo-electric photometer on the market whose accuracy (for measurement in monochromatic light) surpasses that obtained with an ordinary visual photometer. The difficulties are mainly due to fluctuations in the intensity of the light source, fluctuations in the sensitivity of the cell and to the very small currents it is necessary to measure if the intensity of the light is low. The simple photo-electric photometers can only be used with filters, because a monochromator would cut down the intensity too much.[1]

Photo-electric cells can be divided into two classes according to their internal resistance, as this determines the technique employed in their use. Low resistance cells, such as the Weston " Photronic " cell, the Westinghouse copper oxide cell (as well as thermocouples) are used with sensitive galvanometers. For measurements in the visual region, cells are available with a sensitivity curve approximating to that of the eye. For measurements in the infra red, thermocouples are used as well. Owing to their low resistance, no great advantage can be gained by amplification, but as the sensitivity of these cells is usually high, simple and compact photometers can be constructed with them. They are not usually sufficiently sensitive to be used with a monochromator.

High resistance photo-cells consist of a deposit of an alkali metal enclosed in a bulb, which is either evacuated or filled with an inert gas. The gas-filled cells are more sensitive but the vacuum cells are more constant in their characteristics. In either case the currents

[1] Such instruments are made by Messrs Adam Hilger, Ltd., A. Gallenkamp & Co. Ltd., and Salford Electrical Instruments Ltd.

generated are so small that they have to be amplified in order to be measured. For a more detailed description of the various devices used reference should be made to Campbell and Ritchie.[1]

The best method of using amplification is to arrange for the amplified current to adjust two beams of light automatically to equal intensity. In that case neither one of the main objections to photo-electric cells—their liability to alter their sensitivity—nor any alteration of the source of light renders the measurement inaccurate. Hardy [2] used this method first, and a simpler instrument has been used by the author for colorimetric measurements of various kinds. It is of special use for following the reactions of coloured substances in solution, where rapidity of measurement is so essential as to preclude the use of any form of visual photometer.

For use in the ultra-violet, some sort of *photographic photometer* is usually employed. These use the same principles as the visual photometers described above, except that a photographic plate is substituted for the eye of the observer. They can be used in the visible region of the spectrum as well, but their accuracy is not as great as that of photometers using the eye. The search for equality is made on the photographic record using the eye as judge, and the added complication of the photographic plate makes the individual measurement slightly less accurate. If a recording microphotometer is

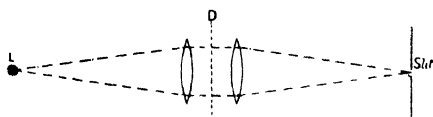



FIG. 135.

available, spectrograms with and without the interposition of the substance being investigated can be taken, and the law governing the blackening of the plate determined by taking a series of spectrograms of the light source after it has been weakened by a known amount. This is most conveniently achieved by placing a diaphragm D as illustrated in Fig. 135 in front of the condensing lens. The light is then weakened by an amount which can be calculated from the dimensions of the diaphragm. As this method depends on the availability of a recording microphotometer, and this instrument is only available in well-equipped physics laboratories, it is not likely to become general.[3]

[1] Campbell and Ritchie, *Photoelectric Cells: their Properties, Use and Applications*, 3rd edition, London, 1934.

[2] Hardy, *J. Opt. Soc. Amer.*, 1935, **25**, 305; Hardy and Cunningham, *E.P.*, 291, 397.

[3] *The Practice of Absorption Spectrophotometry*, Adam Hilger, 1932; *Recent Applications of Absorption Spectrophotometry*, Adam Hilger, 1932.

(*d*) Application of the Colorimetric Methods

Spectrophotometric methods have been used by Formanek[1] for the identification of dyestuffs. He determines the wavelength of the absorption maximum of the dyestuff. This method can be very useful if no coloured impurities are present, but as this condition is seldom fulfilled in practice, the results should be treated with considerable reserve. Although it is improbable that the same maximum will be observed on different dyestuffs, the addition of a coloured impurity can easily shift the position of maximum absorption. The *p*H value of the solution can also determine the position of the maximum. The method should therefore be confined to providing extra evidence of identity and cannot be used as evidence of the presence or absence of a compound. It should also be noted that the source of light and the characteristics of the observer's eye may in some cases shift the maximum by a small amount. It is therefore always advisable not to rely on published data but to compare the unknown solution with a solution of the substance with which it is suspected of being identical. The published data are, however, very useful for the indications they provide.

Technically the method is simple enough. A cell or test-tube containing the solution is placed in front of the slit of the spectroscope and the light source focussed on the slit. It is then possible to observe the maxima by looking at the spectrum. By means of cross wires in the eyepiece they can be located and the wavelength measured. Should the maxima be too broad, the solution is either diluted or the thickness of the cell is reduced. In fact it is always advisable to make the observation at various dilutions because some maxima can only be seen at adequate densities.

If the spectroscope is only used to compare two solutions, a calibration of the wavelength scale is unnecessary. In most cases, however, when a record is required, even if the same instrument is being used, it is always advisable to check the accuracy of the wavelength scale. For this any source of light which emits a line spectrum is suitable. Line spectra are emitted by the salts of alkalis and alkaline earths in the Bunsen flame, and also by electric discharge lamps such as mercury vapour lamps and neon lamps. The accompanying table gives a list of the main lines which can be conveniently used for calibration, with their approximate intensities. Most spectroscopes have a wavelength scale, and it is usually sufficient to set the scale correct to one wavelength by setting it to the most intense line of the spectrum available. It is sometimes convenient to adjust the spectroscope first to the sodium lines (5892 and 5896 Å) and move the prism

[1] Formanek, *Untersuchungen und Nachweis von Farbstoffen auf Spectroskopischen Weg*, Berlin, J. Springer, 1908-1913; Formanek and Knop, *ibid.*, 1926 and 1927.

until the reading for these is correct. As no other lines are obtained by introducing a sodium salt into a Bunsen flame, there can be no doubt about their identity. Then starting from this region, a source

TABLE OF WAVELENGTHS OBSERVABLE IN THREE COMMON SOURCES OF LIGHT SUITABLE FOR USE IN CALIBRATION OF VISUAL SPECTROMETERS

(a) *Sodium Salt in Bunsen flame.*

Wavelength.	Remarks.
589·6 Å.	Yellow doublet.
589·0	Can be resolved by most instruments.

(b) *Mercury Vapour Lamp.*

Wavelength.	Intensity.	Remarks.
690·7	10	Red.
623·4	8	
612·3	6	
607·2	5	
579·1	10	Yellow doublet.
577·0	10	
567·6	5	
546·1	10	Intense green line.
496·0	5	
491·6	5	
435·8	10	Blue triplet.
434·7	6	
433·9	6	
407·8	7	Violet doublet.
404·7	10	

(c) *C/5 Watt Neon Lamp* (" *Beehive* " *Type*). 200 *Volts.*

Wavelength.	Remarks.	Wavelength.	Remarks.
724·5	...	540·0	...
717·3	...	535·8	...
692·9	...	534·1	...
650·6	...	533·0	...
640·2	...	478·8	...
638·2	...	471·5	...
626·6	...	470·9	...
614·3	...	470·4	...
596·5	...	456·7	...
588·1	...	453·8	...
585·2	Most prominent line.		

N.B.—Only the more intense lines are given in the above table.

of light containing a larger number of lines as given in the above table can be used to check the accuracy of the scale over the whole spectrum. In a good instrument the scale when set correctly for one wavelength is usually accurate to about 10 Å for all the others.[1]

[1] Kayser, *Handbuch de Spectroskopie*, Leipzig, 1900-12.

For quantitative analysis the following main conditions must be observed :—

1. No coloured impurities should be present, or, if the observations are made with monochromatic light, no impurity having a noticeable extinction coefficient at that wavelength should be present.
2. No substances should be present that have any effect on the concentration of the coloured substance.

This latter condition can be of considerable importance if the coloured substance is easily converted to other forms by substances that are present. An indicator, for example, would be sensitive to the *p*H value of the solution (photometry of an indicator is often used to determine the exact *p*H value of a solution). Some dyestuffs would be extremely sensitive to reducing agents. The range of substances that may affect some colours is so large that a special investigation into these possibilities is sometimes necessary. In most cases, however, it is sufficient to test Beer's law (*i.e.* the validity of equation (2)) over the range of concentrations used, because dilution with the solvent will usually alter conditions sufficiently to show up any undue sensitivity of the coloured substance. Also, the variation of the concentration of the substances known to be present will soon show whether the coloured substance is suitable for use in quantitative analysis.

The procedure is to determine the extinction coefficient of the substance ; then, if the density of a solution of this substance is determined, the concentration can be calculated according to equation (2).

In order to ensure accuracy, measurements should be made in monochromatic light, the wavelength of which should be as close as possible to the absorption maximum of the substance to be estimated, firstly, because any impurities are less likely to affect the result where the extinction coefficient is a maximum ; secondly, any slight changes in the position of the maximum are less likely to influence the result (such as changes due to difference in *p*H value, etc.).

One of the main points to observe is that a suitable concentration and thickness of solution or too great a thickness result in a very high absorption coefficient and, consequently, a very low intensity of the fields to be matched. Whatever method of comparison is used, the results are likely to be inaccurate. If, on the other hand, too weak a solution is used, or if a thin layer is observed, slight errors in the comparison have a comparatively large effect on the result, *e.g.* if the density of the solution is 1·0 at the concentration and thickness chosen for the measurement, an error of 2 per cent. in the matching of the intensity will cause an error of 0·8 per cent. in the estimation of the

concentration, whereas if a density of 2·0 is measured, the same error of 2 per cent. in the intensity will cause an error of only 0·4 per cent. in the estimation of the concentration. On the other hand, if the same instrument is used, the light intensity will be only one-tenth of its previous value at the density 1·0. At density of 0·1 the accuracy would only be 8 per cent., and the light intensity ten times the value at density 1·0. It is therefore advisable to use as high an intensity as possible. Thus the accuracy obtained with simple instruments using filters instead of monochromators is often higher than that obtainable with a spectrophotometer. Figs. 136 to 138 show the main

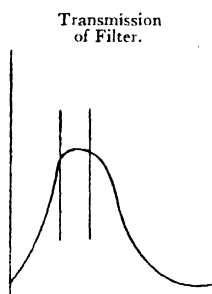



FIG. 136.—Suitable Choice of Filter.

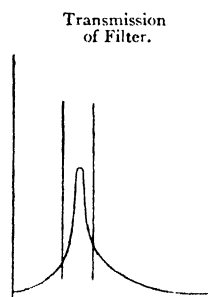



FIG. 137.—Filter transmits too broad a Band.

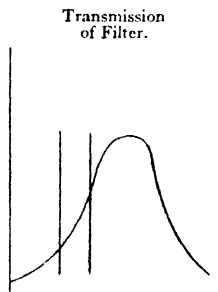



FIG. 138.—Transmission of Filter does not coincide with Absorption Maximum.

considerations to be observed in choosing a filter for a given purpose. If the filter possess too broad a band (Fig. 136), alteration in the density will give rise to alterations in the colour of the fields to be matched ; with consequent inaccuracy, the results depending on the sensitivity of the eye and the spectral distribution of the source of light.

If a number of filters are available, and it is desired to determine which is the most suitable for a given solution, the solution is filled into one side of the Duboscq, the other beaker being left empty or filled with water. The light coming from the side which does not contain the coloured solution is then cut down by some means which cuts down all wavelengths equally, such as a wire gauze or a piece of neutral glass. The filters are then inserted one at a time (so that both beams have to

pass through them), and for each filter the thickness of the coloured solution is adjusted until the two fields appear equal in brightness. The filter for which the thickness is smallest is then the most suitable for use with the liquid in question. In some cases it is convenient to convert the substance, which it is decided to estimate quantitatively, into another coloured substance and estimate this second one. Vat dyestuffs, for example, are readily soluble in sulphuric acid, forming solutions of totally different colour from the original dyestuff. They are not readily soluble in other solvents, but this solution can be conveniently used for photometric determinations. The amount of dyestuff on a given dyeing can be determined by this method, since the sulphuric acid dissolves the cotton forming a solution which is only slightly coloured compared with the dyestuff solution. By dissolving a piece of undyed cloth at the same time, the colour of the cotton in sulphuric acid can be allowed for.

Photometric methods are particularly useful in the case of routine tests, because measurements with a photometer are much more rapid than with a balance. They are also of great value where very small quantities have to be estimated, such as the dye on a few square centimetres of cloth. For general use they often suffer from their great sensitivity, and as a large number of commercial dyestuffs are mixtures of compounds of a similar shade, other chemical methods have to be employed, since this latter condition is the one which renders photometric methods inconclusive.

Determination of the Concentration of Dyestuffs on Fibres

Cellulose Fibres.—In investigations of the relative rates of dyeing of different dyestuffs and different fibres, quantitative evaluation of the concentration of dyestuff on the fibres is important; also, in the investigation of faults quantitative measurements are of great use, since the apparent depth of dyeing can vary with several other factors besides the actual concentration of dyestuff. C. M. Whittaker first drew attention to the effect of fine filament denier viscose having a less apparent depth of shade than coarse filament viscose although the concentration of dyestuff was the same. Other factors also, as for example surface abrasion, can vary the apparent depth of shade.[1] Further, it is sometimes important to decide if, first, an apparent variation in shade of rayon is from unlevel dyeing, and secondly, whether this is from some inherent variation in the yarn; in such a case a quantitative strip and re-dye is indicated.

In the case of acid dyestuffs applied to wool the dye bath can be completely exhausted so that it is not difficult to apply a known quantity

[1] Preston, *Text. Manuf.*, 1936, **62**, 343.

of dyestuff to a known weight of fibres. The position of cellulose fibres is different. Here the dye bath is usually far from completely exhausted, consequently some method of determining the concentration of dyestuffs on the fibres is necessary. Many different classes of dyestuffs are applied to cotton and regenerated cellulose rayon, and the analytical methods suitable for one class cannot be used with another.

Quantitative chemical methods have been used (p. 761), but in many cases these methods cannot be used, either because the constitution of the dyestuff is not known, or because the concentration of dyestuff present is so small that the method is of insufficient accuracy. In such cases colorimetric analysis can be used conveniently. Apart altogether from the question of wide applicability the colorimetric methods are generally more rapid than are the chemical methods. The analytical results obtainable are accurate to about 1 in 100 using visual methods, for all except yellow dyestuffs.[1] This is in accord with the least perceptible brightness step which is about 1 per cent. of the brightness.[2]

The power of the eye to discriminate small differences of colour differs in different parts of the spectrum. Consequently the accuracy with which a particular coloured solution can be measured will depend on the region in the spectrum where its absorption band is situated. M. P. Pelton [3] has investigated this and finds that apart from the dependence on concentration (the least perceptible change is less for dark shades than for pale ones) the estimated just perceptible values for fairly dark shades of the different colours are : yellows 5·4 per cent., oranges 1·7 per cent., reds 1·6 per cent., greens 1·1 per cent. and blues 0·9 per cent.

Direct Dyestuffs on Cellulose Fibres.—A weighed quantity of the dyed fibres is extracted with a known weight of 25 per cent. pyridine in a stopped bottle at room temperature.[4] Alternatively, hot 15 per cent. pyridine can be used for the extraction.[5] For obvious reasons a low degree of accuracy will be obtained if the dyestuff solution is either too light or too dark coloured. An intermediate concentration is best. The weight of fibres extracted and the volume of the solvent should be chosen so that the concentration of dyestuff in solution is 10-20 mg./litre [6] and matched in a layer about 20 mm. thick. Direct dyestuffs vary considerably in the case with which they are extracted from the fibre, thus Chrysophenine G can be

[1] Neale and Stringfellow, *J. Text. Inst.*, 1933, **24**, 145.
[2] *Inter. Crit. Tables*, vol. 1, p. 93.
[3] *Shirley Inst. Mem.*, 1938, **16**, 53.
[4] Neale and Stringfellow, *Trans. Farad. Soc.*, 1933, **22**, 1167.
[5] Boulton, Delph, Fothergill and Morton, *J. Text. Inst.*, 1933, **24**, 115.
[6] Neale, *J. Soc. Dyers and Col.*, 1936, **52**, 252.

extracted with hot water alone. Some dyestuffs, *e.g.* sky blue FF, will be completely extracted with cold pyridine in about 24 hours, whilst others require longer extractions. As soon as the dyestuff is obtained in solution it can be determined by colorimetric comparison in a Duboscq colorimeter using a standard solution of the dyestuff for comparison. If a standard solution is not available then a comparison can be made with a neutral grey solution [1] using a colour filter with a narrow band which just covers the absorption maximum of the dyestuff. Alternatively, comparison can be made using monochromatic light and one of the photometers described above. In either of the two last methods the results can only be expressed in terms of the extinction and not the concentration of the dyestuff. However, if the extinction coefficient is known then the concentration can be calculated.

In many cases neither a standard solution is available nor is the extinction coefficient known. In this case if the information required is the relative concentrations of the same dyestuff on different yarns or fabrics, one of these can be selected as the standard for comparison.

In the case where two dyestuffs have not exactly the same colour as, for example, comparison between a pure and a commercial sample, the use of a contrast colour filter is valuable.

Vat Dyestuffs on Cellulose Fibres.—Some vat dyestuffs can be determined on cellulose fibres by dissolving approximately 50 mg. of the dyed material, which should be quite dry, in 25 ml. of concentrated sulphuric acid. A similar weight of undyed yarn or fabric should be dissolved in sulphuric acid to use in compensating the dyed sample in the colorimeter for the slight yellowing of the sulphuric acid, due to the charring of the cellulose in the dyed sample. Comparison can then be made against a standard solution of the vat dyestuff in sulphuric acid or against a neutral grey solution as described above for direct dyestuffs.[2]

There is also the possibility of using ethylene diamine as a solvent for extracting the vat dyestuff in a manner similar to the use of pyridine solution for extracting direct dyestuffs.

Dyeings on Cellulose Acetate Rayon.—Both rayon and dyestuff can in most cases be dissolved in a solvent such as acetone or glacial acetic acid and the dyestuff can be determined colorimetrically as described above.

Measurement of the Colour of Fabrics.—The measurement of the colour of solutions either in terms of a colorimetric standard, or

[1] A. Thiel and W. Thiel, *Leitz Bulletin*, No. 4 micro 1933; A. Thiel and Diehl, *Sitzungsber. d. Gesell. 3. beförderung d. gesam. Naturwissen.*, 1932, **68**, 10; Guelke, *J. Soc Dyers and Col.*, 1934, **50**, 77.

[2] Fitzsimons, *M.Sc. Tech. Thesis*, Vict. Univ., May 1933.

spectrophotometrically, is comparatively simple, because the measurement can be made for transmitted light through a known thickness of liquid. Quite a different state of affairs exists with dyed fabrics. Here the measurement must be made of the light reflected from the surface. This introduces several difficulties. Firstly, the structure of the fabric in relation to the mode of illumination and viewing direction affects the colour. Secondly, the intensity of the reflected light is comparatively low. Consequently, measurement is made much more difficult. However, there are a number of methods and instruments available which more or less satisfactorily overcome these difficulties (*vide* pp. 777 and 785).

Spectrophotometers.—In determining the colour of a surface, the physical property which is of importance is the reflection power of the surface for light of all wavelengths in the visible spectrum. The spectral reflection curve thus forms an unambiguous specification, being independent of the nature of the illumination and of the properties of the eye. It is not strictly speaking a specification of " colour " since there can be no " colour " without human vision, but it is commonly referred to as " colour."

The measurement of the colour of fabrics is complicated by the structure of the fabric, which often causes the colour to be dependent on the direction of illumination and of viewing. Moreover, the intensity of the reflected light is usually comparatively small, whereby measurements are made more difficult.

The influence of surface structure may be overcome by rotating the sample, keeping constant the direction of illumination and of reflection. This gives an average of the intensity of reflection for the given angle of incidence and reflection. The difficulty may also be overcome by employing either completely diffuse illumination or diffuse reflection, the two methods being optically identical. The rotation and the diffusion methods are not identical, but with most fabrics give very similar results.

The determination of the absolute reflecting power of a surface is somewhat difficult, and it is customary to measure the reflection relative to a standard white surface. For this purpose a thick layer of magnesium oxide is usually employed, but magnesium carbonate, baryta and other " whites " are used. As there are slight differences in the reflecting power of these materials, the nature of the standard always should be stated.

A complete determination of the spectrophotometric curve involves measurements at some 30 wavelengths, but for many industrial purposes a smaller number will often suffice. The automatic apparatus of Hardy and others already referred to is ideal, giving in effect an infinite number of points, and in recent years these instruments have

been used in textile colour problems, for example, in the study of colour tolerances. A complete spectral reflection curve can be converted into I.C.I. or C.I.E. trichromatic units.[1] As the process is rather tedious, suggestions have been made for reducing the amount of computation.[2]

Approximate Spectrophotometry.—The determination of reflection at a limited number of points in the spectrum has led to the production of several instruments by textile workers. Usually 7 or 8 narrow spectral bands are used, these being obtained by means of filters. Appel [3] employed a visual instrument in problems of fading, whilst Cunliffe and Farrow [4] use a photographic plate in place of the eye. The " Photocolorimeter " of Toussaint [5] also uses filters, but in this instrument a photoelectric cell and galvanometer combination form the detector. It will readily be understood that as filters pass a band of light and not a single wavelength when used with a filament lamp, the accuracy cannot be so great as with a spectrophotometer.

Trichromatic Colorimeters.—Thomas Young showed that all colours can be produced as a mixture of three, or, at most, four primary stimuli. This fact makes it possible to describe a shade by means of three numbers representing the magnitude of these stimuli. In order to create a standard for purposes of comparison, the International Committee on Illumination have agreed upon definite values for the stimuli and a method of their graphical representation in the colour triangle.[6, 7] By using this system, a shade can be described in three numbers and a letter indicating the light source. Instruments for measuring these values are the Guild colorimeter (Adam Hilger Ltd.), the Donaldson Colorimeter (Bellingham and Stanley, Adam Hilger), and an attachment to the " Leifo " photometer (E. Leitz). A number of specimens which have been measured on the Guild instrument together with the results have been published by the British Colour Council.[8]

To obtain a system capable of specifying a colour in this manner two independent definitions have to be made. Firstly, a " standard observer " must be defined in such a manner that the trichromatic coefficients of any combination of wavelengths which reach the eye of such an observer can be determined. Secondly, for all coloured

[1] Smith and Guild, *Trans. Optical Soc.*, 1931-32, **33**, 73.

[2] Hardy, *Handbook of Colorimetry*, Massachusetts Institute of Technology, 1936; Holmes, *Proc. Phys. Soc.*, 1935, **47**, pt. 3.

[3] Appel, *American Dyest. Rep.*, *Sample Swatch Quarterly*, 23rd January 1928.

[4] Cunliffe and Farrow, *J. Text. Inst.*, 1927, **18**, T 291.

[5] Desbleds, *J. Soc. Dyers and Col.*, 1928, **44**, 327.

[6] Judd, *J. Opt. Soc. Amer.*, 1933, **23**, 359.

[7] Nutting, *Text. Research*, 1935, **6**, 7, 104.

[8] British Colour Council, *Dictionary of Colour Standards*, 1934.

substances (as distinct from illuminants) the conditions of illumination and the characteristics of the illuminant must also be described.

The properties of the "standard observer" are described by giving the co-ordinates of monochromatic light of all wavelengths in terms of the primary stimuli. This can be done in the form of a curve or as a table (both are given by Judd, *loc. cit.*). The agreement between the properties of the "standard observer" and actual observers has been ensured in the I.C.I. system by basing the values on the work of Wright [1] on 10 and of Guild on 7 normal trichromats.

The conditions of the illumination which have been standardized for surfaces are as follows :—

The surface should be illuminated at an angle of 45° and the colour observed at right angles to the plane of the surface.

The following three illuminants have been standardized :—

Illuminant A. "A gas-filled lamp of colour temperature 2848° K."

Illuminant B. The same lamp used with a liquid filter consisting of 1 cm. of each of the following solutions B_1 and B_2.

Illuminant C. The same lamp as for illuminant A used with a liquid filter consisting of 1 cm. of each of the following solutions C_1 and C_2 :—

	Solution B_1	Solution C_1
Copper sulphate ($CuSO_45H_2O$) . .	2·452 g.	3·412 g.
Mannite ($C_6H_8(OH)_6$) . . .	2·452 g.	3·412 g.
Pyridine (C_5H_5N)	30·0 ml.	30·0 ml.
Distilled water to make . . .	1000 ml.	1000 ml.

	Solution B_2	Solution C_2
Cobalt ammonium sulphate—		
($CoSO_4(NH_4)_2SO_46H_2O$) . . .	21·71 g.	30·580 g.
Copper sulphate ($CuSO_45H_2O$) . .	16·11 g.	22·520 g.
Sulphuric acid (density 1·835) . .	10·0 ml.	10·0 ml.
Distilled water to make . . .	1000 ml.	1000 ml.

Illuminant A is used when the colour to be examined will be used in artificial light.

Illuminant B approximates to noon sunlight (4800° K).

Illuminant C approximates to average daylight (6500° K), and should be used when the colour to be examined will be used in daylight.

From the trichromatic match three figures are obtained representing the content of the light reflected in terms of the primary stimuli.

The three figures do not completely describe the optical behaviour of the sample, and the fact that two samples give identical results does not mean that these two samples will have the same appearance with all illuminants. To ensure identity under all conditions,

[1] *Med. Res. Council Spec. Rep.*, 139, 1929, H.M.S.O., London.

they should have the same reflection coefficients as measured in a reflection photometer for the whole of the visible spectrum.

It is possible to calculate the trichromatic coefficients for any illuminant from the spectrophotometric curve. An instrument to facilitate this calculation has been designed by Hardy.

In spite of the sensitivity of the trichromatic co-ordinates to the colour of the light source, such data are valuable. The value lies in the comparatively ready comprehension of the data, which are directly related to the psychological sensations of colour. Spectrophotometric curves on the other hand cannot be comprehended so easily. The fine colour differences between different spectrophotometric curves cannot be visualized although large differences can be (*e.g.* there is no difficulty in identifying the corresponding curves and colours in a pure green or a pure yellow).

The high cost of a trichromatic colorimeter and the skill required to use and maintain it have been serious handicaps in the application of colorimetry to textile problems. The difficulty is not so much the measurement of colour, whether in the trichromatic system or in any other system but in the use to which the results are to be put, other than simply that of a record. Cunliffe and Lambert [1] in 1929 showed how the Guild colorimeter, the spectrophotometer and the Lovibond Tintometer could be used to record the fading of dyed wool fabrics, and in subsequent papers attempted to obtain a numerical expression to represent the degree of fading. They suggested that the ideal method would be to express the degree of fading as the number of just perceptible steps which could be placed between the two colours.

Several attempts along these lines have been made, among which may be mentioned that of Judd [2] who uses trichromatic co-ordinates based on equal sensation steps and of Dorothy Nickerson [3] who transformed data of Nutting [4] to the hue-value-chrome factors of the Munsell system [5] and derived an equation in terms of these factors to represent equal visual steps.

The practical dyer is concerned with the amount of dye which he must use to obtain a definite colour on his material. Attempts have been made to call in the aid of colorimetry on this problem, but it must be confessed that it is as yet of limited assistance.

The Lovibond Tintometer [6] is based on subtractive trichromatic principles and is used to record the colour of textile materials in

[1] Cunliffe and Lambert, *J. Soc. Dyers and Col.*, 1929, **45**, 305.
[2] Judd, *Bur. of Standards, J. Research*, 1935, **14**, 41.
[3] Nickerson, *Text. Research*, 1935-36, **6**, 505.
[4] Nutting, *Text. Research*, 1935-36, **6**, 104.
[5] Munsell, *Munsell Book of Colour*, Munsell Colour Co., Baltimore, 1929.
[6] Lovibond Tintometer Co., Salisbury.

terms of red, yellow and blue glasses. These glasses are so calibrated that a combination of the same scale number of each colour produces a neutral grey when the three glasses are placed together, while the deeper the colour the higher is the scale number. The numerical results are readily understood since dyeing is also a subtractive process.

Attention may also be drawn to a " Photometer of Special Application to Routine Textile Measurements." [1]

Colour Atlases.—Apart from the spectrophotometric and trichromatic co-ordinate descriptions of colours, there are certain semi-empirical colour systems which have a psychological basis. The Ostwald system (*Colour Science*, Wilhelm Ostwald, trans. by J. Scott Taylor, Parts I and II, Windsor and Newton. *The Ostwald Colour Album*, Windsor and Newton, the *Munsell Book of Colour* (Munsell Colour Co., Baltimore, 1929), and the Maerz and Paul *Dictionary of Colour* (McGraw Hill Book Co., 1930-) have colour elements arranged with approximately equal psychological steps. Hence colours may be described in terms of the co-ordinates of these atlases. Similarly, the differences between colours can be defined in units which make some approach to an accurate description of the sensations they evoke.

Colour Matching Tolerance.—The permissible variations or tolerance in colour matching are a matter of personal judgment, the accuracy of which will vary with the experience of the examiner.[2] But perhaps of even greater importance are the conditions of matching. The samples must be juxtaposed since the critical faculty diminishes rapidly as the samples are separated. The light used should be diffuse (to avoid excessive specular reflection) and have a reasonably uniform energy spectrum, *e.g.* north sky light.

Brightness deviations are more tolerable than true deviations ; a classical application is the blueing of " white " fabrics.

Investigations of samples with the Hardy Spectrophotometer (q.v.) by W. P. and E. R. Cohoe [3] were made and the results compared with the judgments of colour matchers. A deviation of less than 5 per cent. in light reflection would be classed as a good match, whilst more than a 10 per cent. deviation would be called a bad match. A fundamentally more accurate method of specifying tolerances is outlined by D. Nickerson.[4]

Daylight Matching Lamps.—The ideal light should be an approximation to north sky light. However, as a filament electric lamp is mostly used as the source, to filter this down to a corresponding

[1] Hampson and Richards, *J. Text. Inst.*, 1934, **25**, T 106.
[2] Pierce, *The Selection of Colour Workers*, Pitman, 1934.
[3] *Ind. Eng. Chem.* (*Anal.*), 1932, **4**, 112.
[4] *Text. Research*, 1935, **6**, 505.

spectral emission means too great a loss of light. Most "daylight" lamps compromise by imitating sunlight.[1] This light is comparatively yellowish, but is a decided improvement on unfiltered artificial light. However, some of the commercial daylight lamps claim to give a light which is a good imitation of daylight from an overcast, or clouded sky, and less yellow than sunlight. Such are the Lamplough Matching lamp which uses filtered tungsten filament electric light, and the Claudegen Artificial Daylight which uses the unfiltered light from a CO_2 gas discharge tube. As well as correct spectral composition, the light should be properly diffused since a concentrated source gives very disturbing lustre and shadow appearances. Far less attention has been given to the light distribution than to spectral distribution, though it is quite as important. The best colour matching installations the writer has seen have been fitted with daylight lamps arranged round the boundaries of the ceiling. On a small scale indirect lighting produces the same effect more conveniently.

Relation of Dyestuff Concentration to Colour of Fabrics.—The relation of the colour of a fabric to the dyestuff concentration is far from simple. Apart from the complication of the fabric structure, and with the simplest arrangement of parallel fibres lying in one plane, the relation is complex. Investigations have been made by:—R. Guelke and M. Fitzsimons (*Trans. Farad. Soc.*, 1934, **30**, 512); R. D. Nutting (*Amer. Dyestuff Reporter*, 1936, **25**, 585); P. S. Tsien (*M.Sc. Tech. Thesis*, Victoria Univ., April 1937). Reference should be made to these papers for further information.

X. TESTING BY FLUORESCENCE

By J. A. RADLEY, M.Sc. (Lond.), A.I.C.

WHEN irradiated with ultra-violet light many substances glow or "fluoresce." If this glow persists after the exciting radiation is cut off, the phenomenon is known as "phosphorescence," the term "fluorescence" being applied to cases where the glow disappears with the termination of the irradiation with the "exciting" light. The phenomenon is due to the molecules of the excited substance absorbing radiation of one wavelength and then becoming deactivated by emitting radiation of, generally, a longer wavelength.

The characteristic fluorescence shown by various substances may change due to physical or chemical change in the substance, for example by exposure to light or by oxidation on exposure to air. These changes may vary from a change in the intensity of fluorescence, often seen when this is brought about by light, to a change in fluores-

[1] Cunliffe and Lanigan, *J. Text. Inst.*, 1929, **20**, T 31.

cence colour, for example those colour changes seen when acid or alkali acts upon certain substances.

The fluorescence may be due to traces of impurities present, a good example of this being the intense fluorescence shown by mineral oils which fluoresce by reason of a small amount of highly condensed organic compounds present, but, on the other hand, a small amount of impurity may inhibit the fluorescence.

It is proposed to consider very briefly the apparatus and technique for carrying out tests in the textile trade together with a few precautions to be taken in special cases. For a description of the general technique the reader is referred to the volume, *Fluorescence Analysis in Ultra-Violet Light*, by the writer and J. Grant (London, 1939).

Precautions. Results obtained from the examination of textiles may be unreliable for one of the following reasons :—

1. The material may be dressed with substances which mask or alter the colour of the fluorescence.
2. Dyestuffs present may mask a particular fluorescence effect shown by the textile itself.
3. Ageing in air or exposure to light sometimes affects the fluorescence.
4. The same fluorescence colour may be shown by a number of substances.
5. The filters used may have different transmission spectra. Some filters let through a certain amount of red light, others allow a portion of the violet end of the spectrum to pass, so that the final fluorescence colours observed have these shades superimposed on them.

Whenever possible blank experiments on reagents should be made and the appearance of unknown samples in ultra-violet light compared with that of samples of known origin treated in known ways.

The unfiltered rays from the lamp should not be allowed to reach the eye, either directly or by reflection, but the filtered light is perfectly safe to work with, although for long periods and in conjunction with the ozone given off by the lamp it induces headache in some workers.

The Source of Ultra-Violet Light

This rests mainly with the investigator, but most recent workers prefer the quartz mercury vapour lamp which is efficient, easy to use, and has several advantages over the arc lamp type employing carbon, iron or tungsten electrodes.

The visible light from the lamp would mask the fluorescence of the substance under examination, and to eliminate this visible light the rays from the lamp are passed through a dark filter. To-day these

are invariably made of a black glass containing nickel oxide. After passing through this filter only ultra-violet light is present, although in most filters a little purple or a little red light is also passed. For most purposes, however, this is so weak as to constitute no disadvantage to actual observation, but must be taken into account when comparing results with those obtained by other workers. Several lamps are on the market for fluorescence testing in which the arc tube is totally enclosed in a housing fitted with a window made of the nickel oxide glass: of these the Hanovia Analytic lamp is probably the best known, and for textile work the hanging type, which casts a wide beam of light, is best.

The lamp when first switched on takes a few minutes to attain its maximum output of ultra-violet light, and before making any observations it is well to allow this period to elapse. When the lamp is switched off it may sometimes be again required within a minute or two, but it will be found that it does not light immediately. This type of lamp needs to be cool before it will start.

It is preferable, where possible, to allow enough tests to accumulate, since to obtain the best value from fluorescence tests they should be carried out in a darkened room and the eye should be allowed to become accustomed to the darkness before making any observations. A much greater differentiation between fluorescence colours and intensities is thus attained. Many substances do not fluoresce but appear a dull purple colour under the lamp, as they reflect the violet light which passes through the filter together with the ultra-violet light. To overcome the deceptive appearance which this gives the substance should be viewed obliquely as well as directly at right angles as usual. Comparative tests should be carried out wherever possible. With fabrics, the dressing materials and the dyestuffs may completely mask or alter their fluorescence colours. The evidence of the lamp should be considered in conjunction with other physical and chemical tests before arriving at a decision, and when occasionally the evidence is contradictory, it is preferable to reject that of the lamp. Used carefully and with discrimination the lamp gives valuable *indicative* information.

Examination of Materials

Lump material is examined under the lamp and also the face of a fresh fracture of the material. Any difference is probably due to the action of air alone or combined with the action of light. The freshly broken surface is spotted with $N/1$ sulphuric acid, $N/1$ caustic soda and distilled water and the three spots examined. The material may next be ground to a powder and blown on a damp filter paper and this examined together with some of the dry powder retained for the purpose.

Solutions of substances sometimes show a difference in fluorescence

when the solvent is changed. One portion of an aqueous solution may be made acid, another made alkaline, while a third portion is kept neutral, and these solutions examined under the lamp. The fluorescence colour of the meniscus and of the body of the liquid should be observed. A bright zone at the meniscus is often observed, and as the solution is diluted with more solvent this zone extends down the tube until the whole of the liquid in the tube glows. These points may be demonstrated by examining 10 per cent. and 0·1 per cent. solutions of Rhodamine B 500 in water and alcohol, when it is seen that the concentrated solutions show little or no fluorescence, or only at the meniscus, whereas the *whole* of the liquid fluoresces brilliantly in the dilute solutions. It will also be seen that the weak fluorescence in water is enhanced by the addition of 10 per cent. of a 30 per cent. acetic acid. An acid solution of fluorescein is non-fluorescent, whereas a neutral or alkaline solution is highly fluorescent. Among non-fluorescent solvents for use in this work may be mentioned chloroform, benzene, solvent naphtha, alcohol and ether, all, of course, in a fairly pure condition.

The method of capillary analysis is very useful and delicate. Filter paper strips, 2 to 3 cm. wide and some 30 cm. long, are suspended so that 5 mm. of the lower end just dips into the solution under examination and the whole set aside in a cool place entirely free from draughts for twelve to twenty-four hours. At the end of this time the liquid has crept up the filter paper and well-defined zones are sometimes formed. Examination of these strips under the lamp often gives valuable information, more particularly when dealing with complex mixtures. Acid, alkaline and neutral solutions should be examined in this way, and if the intensity of fluorescence of the zones is measured with a photometer they can be plotted against the distance of the zone from the top end of the paper strip and a characteristic graph obtained for each substance in each medium.

Liquids are examined in the same manner as solutions and, in addition, boiling under the lamp in a test-tube of non-fluorescent Kavalier glass is often carried out, the fluorescence of the body of the liquid, the meniscus and of the condensed droplets farther up the tube being noted. Test-tubes made of non-fluorescent glass should be chosen for this type of work. Allowing a drop of the liquid to run down a plate of non-fluorescent glass backed with black paper or enclosing a drop of the liquid between two thin glass slides and examining under the lamp are other methods used.

Photographic Methods. To record and demonstrate observed fluorescence effects photography can be invaluable. The photograph of the fluorescence shown by an object is generally termed a " luminogram," while " ultra-violet light photograph " is the term applied to

one which shows the ultra-violet light reflected from the object but not the fluorescent light it emits.

To obtain *luminograms* the object is illuminated by filtered ultra-violet light and photographed with any ordinary camera, in front of the lens of which is placed a glass-sided cell 1 cm. thick containing a 2 per cent. solution of sodium nitrite or a 1 per cent. cerium ammonium nitrate solution to cut out any reflected ultra-violet light. A small cell containing one of these liquids which can be fitted on to the lens of the camera has been suggested and used by Dr Ainsworth-Mitchell with success. Panchromatic plates are used for ordinary work, and by use of the modern triple layer colour films, or by the three-colour process, luminograms in natural colours may be obtained.

To obtain ultra-violet light photographs the camera must be fitted with a quartz optical system in front of which is placed a filter which passes ultra-violet but retains the visible light. The filter can therefore be removed from the ultra-violet lamp and placed in front of the camera. The entire light from the lamp falls on the object, and the fluorescence light together with the visible light from the lamp reflected by the object is absorbed by the filter in front of the camera lens, whilst the reflected ultra-violet light passes and is recorded on the photographic plate.

The plates used should be panchromatic, and G. W. Harrison [1] has applied various oils which fluoresce in ultra-violet light to give a thin coating on the plate in order to make it more sensitive when illuminated with light of wavelengths between 2200 and 3800 Å. He employed the Cramer Contrast Process, Seed 23 and Wellington Super Xtreme plates, and found that the degree of change in the sensitiveness depends on variations in the thickness of the oil film and the coating. The greatest sensitiveness was found with a clear paraffin oil and a contrast plate, whilst the greatest contrast was given by a light lubricating oil.

The length of exposure in any particular case must be determined by trial, but the intensity of the fluorescence gives some guide to this. After a little practice the method is easy to use and the results justify the work expended in mastering the technique.

Quantitative Examination. It is difficult to describe colours which are very similar and vary only slightly in shade and intensity and would take much time and space to record; even then it is not certain that a colour described could be compared with another observed some time later. Hence some apparatus is required to clarify results for recording purposes. In using the spectroscope to record visible fluorescence colours no quartz prisms or lens are required. The object is mounted in front of the slit and an intense beam of ultra-violet light concentrated on it by means of a quartz lens or a

[1] *J. Opt. Soc. Amer.*, 1925, 11, 113.

water lens. By using a spectrophotometer or a spectrograph in conjunction with a photometer the intensity of fluorescence in each portion of the spectrum is obtained. By plotting the intensity of fluorescence at different wavelengths against the corresponding wavelength as abscissa characteristic curves are obtained. If the spectrum is photographed a filter should be interposed between the object and the slit to cut out any reflected ultra-violet light which might fog the photographic plate.

For use in factory work, instruments giving readings in the three primary colours are preferable. The Lovibond tintometer can be used in the normal manner or, preferably, a colorimeter of the Guild or of the Donaldson type can be used (*cf.* Colorimetry, p. 794). To use these instruments the sample is placed in a holder in front of the aperture of the comparator and a beam of ultra-violet light directed on to it. On viewing through the eyepiece the fluorescence colour is seen in one half of the field of vision and the filters are adjusted until the two portions of field of vision are equal in intensity and colour. The filters are then read off and may be recorded. The values obtained for a certain yellow colour will read "red 27, green 44, blue 29," whilst a buff colour could be recorded as "red 53, green 31, blue 16."

Differentiation of Textile Fibres

It is often possible to distinguish between various textile fibres, or different grades of the same fibre, by means of the fluorescence in ultra-violet light, but it is not often that such a means need be used as other very simple tests are available.

In general, vegetable fibres show a yellowish fluorescence which, after the usual treatments to which textiles are subjected, *i.e.* scouring, bleaching, etc., changes to dull tones of blue and violet. Fibres of animal origin when cleaned after shearing or plucking show strong blue fluorescence tones, and of the individual textile materials bleached wool shows the strongest fluorescence. Degummed natural silk and unbleached but light-coloured wool show a blue fluorescence, the intensity of which is less than that of the bleached wool, and these are followed in order of decreasing intensity of fluorescence by mercerized and bleached cotton, acetate rayon and raw cotton.

Cotton. An examination of the various grades of cotton under the lamp offers no advantage whatever over a visual examination in daylight. Physical differences in cellulose appear to be without any marked effect on the fluorescence shown. Impurities in the cotton such as dirt, which affect its colour and appearance in daylight, play an important part by influencing its appearance under the lamp, and in the presence of dyestuffs this appearance can be vastly modified.

The examination of cotton, if this is desired, is best carried out on a carded yarn in which the fibres have been smoothed and lie parallel in the sample. The colours of cottons from different sources will be found to appear from white with a yellow tinge to a decided brown with purple reflections.

The treatment which a cotton has received often affects the fluorescence; thus, boiling with alkali dulls the fluorescence colour, and this change is most marked with mercerized but unbleached cotton. Nopitsch considers that brightness and the shade of the fluorescence colour in this case are especially dependent on the degree of stretching in mercerizing which causes a loss in brightness and a tendency of the colour tone to move towards the violet.

Splashes of hard water which have dried on a cop of raw cotton cause the appearance of greyish purple non-fluorescent spots visible under the lamp, while oil spots from dirty machinery are easily detectable. Sometimes wetting agents are employed in damping the yarn as it comes from the spinning machine, and if this is carried out by spraying the cops they are sometimes detectable by a border zone fluorescing in a lighter colour than the unwetted part. If the raw yarn is wetted in a steeping solution and dried without further rinsing some threads are more luminous than others.

Bleached cotton, especially if glossed, appears duller than raw yarns, but on mercerization the fluorescence is again increased, but the shade of fluorescence is different. Imitation Mako yarn obtained by dyeing can be distinguished from genuine Mako yarn by the different fluorescence colour it shows under the lamp.

Linen and Hemp. Both these fibres appear a yellowish grey colour under the lamp and are much duller in appearance than raw cotton, and cannot be distinguished from each other, or from jute, by fluorescence. Bleached linen yarn shows a yellowish white fluorescence of a similar intensity to that of mercerized cotton, and bleached linen fabric shows a much yellower fluorescence than bleached cotton fabric. Although jute cannot be readily distinguished by its fluorescence from the other yarns the violet colour under the lamp obtained with jute from many sources disappears after extraction with petroleum ether, as mineral oil is widely used in the treatment of jute, and, as this is not used with the other fibres mentioned, it is more or less characteristic for jute. Many unbleached kapoks examined by Nopitsch showed a full sulphur-yellow fluorescence without any bluish light in the shadows. Loose ramie also shows a yellow fluorescence somewhat redder in shade than that of kapok.

Wool and Animal Hairs. The keratin in wool and hair shows a bright blue fluorescence. In hair the fluorescence is modified by the colouring matter present, black hair being non-fluorescent and white

hair brightly fluorescent. The blue fluorescence of wool is often masked by dirt and fats, etc., when the wool is in the raw state, but appears when these are removed by solvents. This blue fluorescence is intensified with increased washing, while with cotton it is diminished.

The fluorescence of wool is dulled increasingly with increase in length of time of exposure to sunlight or ultra-violet light, so that after several weeks the fluorescence may change from bright blue to a dull reddish blue. When examining wool it should be also remembered that oils used in lubricating the yarn may modify the fluorescence.

The action of small amounts of caustic soda on wool tends to decrease the intensity of the fluorescence, and if after the initial fall the amount of alkali be increased, no further difference in the fluorescence is noticed. The normal chlorination of wool, using 1° Tw. sodium hypochlorite solution, reduces the intensity a little, while treatment with 5° Tw. definitely decreases the intensity of the fluorescence.

W. Sieber[1] gives a method whereby chemical and mechanical damage in wool can be detected. The sample to be examined is wetted-out with hot water and then immersed in a boiling 1 per cent. solution of Benzopurpurine 10 BS for five minutes, removed, rinsed and examined under the lamp. Undamaged wool gives the usual bluish fluorescence, while mechanically damaged wool appears pink, wool attacked by alkali and acid appears yellowish pink to red or bluish pink to red, respectively. These colour reactions can be seen in daylight but are more apparent under the lamp.

Mohair appears bluish white and cannot be differentiated from wool, while white calf and cow hair appear more violet, bleached pig bristles showing a bluish white colour.

Natural Silk. Raw silks (*e.g.* yellow Italian Grege) have a yellow fluorescence and there appears some evidence that the colour of the fluorescence under the lamp bears some relation to the colour of the raw silk in daylight. Degummed silk, however (*e.g.* degummed Organzin silk), shows a very bright pale bluish fluorescence much brighter and whiter than that shown by acetate rayon. Even after degumming some silks show a yellowish colour and have a slight dull yellowish fluorescence under the lamp. In one laboratory it was found that all the breaks that occurred in degummed silks took place in these yellow portions and their appearance may be due to bacterial action on the bast.

Artificial Silks or Rayons. Provided undyed and unsized fibres are used certain distinctions may be made between the various types of artificial fibres now marketed, but many are treated with various oils, etc., during the finishing processes and therefore should be given a mild scour or extraction, although even this introduces complications

[1] *Textilber.*, 1928, **9**, 753.

in many cases. It would not appear that the lamp is sufficiently safe as a means of distinguishing between artificial fibres of the same type.

Bemberg rayons give a reddish white fluorescence rather opalescent in appearance, with strong bluish or bluish violet reflections, whereas viscose rayons have a yellow tone with bluish shadows. Nitro rayons have a pronounced flesh-coloured fluorescence which is much redder in tone than that shown by the viscose type.

Acetate rayons show a brighter fluorescence than the above, the colour being blue violet to violet. Sthenose, which is a rayon after-treated with formaldehyde, shows a yellow tinge without the bluish shadows shown by viscose rayons.

Viscose may be distinguished from cellulose acetate by dipping in a hot 1 per cent. solution of Acronol Yellow TS or Thioflavin T for a few seconds and, after rinsing very thoroughly and drying, examining under the lamp.[1] A brilliant greenish blue to blue fluorescence is shown by cellulose acetate whereas the viscose appears a bright yellowish green colour.

Bemberg rayon can be distinguished from viscose rayon by the following treatment devised by the writer.[2] A cold 0·2 per cent. solution of Acronol Yellow TS is made in a mixture of equal parts of water and methylated spirits to which 5 ml. of a 10 per cent. sodium carbonate solution has been added and the solution boiled and cooled. The sample to be examined is immersed for two minutes in the cold solution and then thoroughly rinsed in cold water and examined under the lamp. The viscose appears a dull purple or dull blue, whereas Bemberg silk appears a brilliant bluish or yellowish white according to the state of dryness of the sample and the time elapsing between the treatment and examination of the sample.

If cellulose acetate is dipped for a second or two in the above reagent, rinsed and examined, it shows a most vivid deep blue colour which is very striking, and easily distinguishes it from the colours shown by either viscose or Bemberg rayons. In these tests it will be noted that the fabrics are examined in the wet state. If dried the intensity of the fluorescence is somewhat diminished, but the colours are slightly more distinctive.

Another test devised by the writer for distinguishing between Bemberg and viscose materials is carried out by " dyeing " the sample at 85° for five minutes with Primuline AS, using a 1 per cent. shade and a 30 to 1 liquor. Prior to entering the sample in the dye-bath, concentrated sulphuric acid, to the extent of 5 per cent. on the weight of the hank, is added to the liquor. After rinsing the viscose shows

[1] Haitinger, *Mikrochemie*, 1935, **16**, 321.
[2] Radley, *Analyst*, 1938, **63**, 266.

a bright blue fluorescence under the lamp, whereas the fluorescence of the Bemberg material is golden yellow.

The fluorescence of artificial silks is unaffected by extraction with petroleum ether, but after treatment with 96 per cent. alcohol the fluorescence of cellulose acetate changes to yellowish grey in colour and is less intense. Bemberg and viscose rayons show no change when scoured in a 0·5 per cent. soap and 0·5 per cent. ammonia solution, but that of cellulose acetate is paler and less blue. The fluorescence of Bemberg rayon changes to grey and then reddish violet when treated with caustic soda of sp. gr. 1·008, but that of viscose is unaffected by this treatment. The fluorescence of cellulose acetate under these conditions changes to a pale yellow.

Mixed Fabrics. Cotton and linen can be distinguished from half linen especially if the edges of the fabric are frayed and examined under the lamp. Raw half-wool fabrics often allow the cotton to be detected by the less intense fluorescence these threads show as compared with the wool, *e.g.* wool-fibro does not appear so bright as wool delaine but exhibits the same shade of fluorescence colour and tiny dark spots show where the cotton fibres are exposed. By means of the reagents above, used in conjunction with a microscope and the lamp, mixtures of viscose, Bemberg and cellulose acetate rayons one with another can be detected.

Colouring Matters

It may be fairly definitely stated that the lamp cannot be used to *identify* colouring matters, although in a number of cases it is sufficient to characterize them, showing to which of Green's tables the colour belongs.

For examination the dyestuff may be dyed on as many materials to which it can be applied or dissolved in water or in alcohol, as these solutions often show the same fluorescence as the dyed fabric. If the dyestuff is already on the fabric it may be extracted with a suitable solvent, *e.g.* alcohol for basic colours and ethylenediamine, pyridine or cyclohexanol for vat colours. Solutions in benzene of certain vat colours such as Durindone Pink FB, FF and Durindone Red B and 3B, Caledon Brilliant Purple R, 2R and 4R, Caledon Dark Blue RRD and G, Caledon Navy Blue R show fairly strong fluorescence in daylight, and in ultra-violet light the fluorescence colours are brilliant. The fluorescence colours vary from yellowish red or orange to blood red and cannot be used alone to differentiate between closely related colours. In general, no fluorescence appears to be shown by the solution of the leuco body in the alkaline hydrosulphite solution, since alkaline hydrosulphite solution absorbs the ultra-violet rays so that they never reach the leuco body ; hydrosulphites can also deactivate a number of fluorescing compounds.

Derivatives of quinoline, acridine, phthalein, primuline and thioflavine generally show a strong and characteristic fluorescence in aqueous or alcoholic solution. Dyestuffs containing a S-group or a thiazole ring also show a very strong fluorescence. Many benzene substitution products and azo dyestuffs containing benzene nuclei show no fluorescence, whereas the corresponding naphthalene compounds fluoresce strongly.[1] The only fluorescent colours of nitro-derivatives are those obtained by diazotization and coupling with compounds which are already fluorescent. The nitro-group depresses the fluorescence to a very great extent, as also sometimes does the hydroxyl group, but, to a lesser extent, the formation of an alkali salt often increasing the fluorescence.

The usual limits between which many dyestuffs fluoresce when fixed on the fibre is generally of the order of 0·01 to 5 per cent. The colour of the fluorescence depends on the concentration, since the emitted light undergoes selective absorption by the dyestuff itself. The effect of this absorption varies with the concentration and is a confusing factor.

The majority of dyestuffs do not fluoresce in the solid state, and when materials are dyed the natural fluorescence shown by the substratum is repressed so that the dyeing appears a dark purple or dull-reddish colour under the lamp. In very pale shades some fluorescence of the substratum takes place but is modified by the colour with which it is dyed. A greenish-yellow colour which is not fluorescent if dyed on wool in heavy shades will appear dirty violet brown, and in light shades a weak greenish shade, whereas a blue dyestuff, which appears inert in strong shades, in a weak shade will often appear pale blue due to the blue colour of the fluorescence of the wool being transmitted through the blue dyestuff.

Browns, greens and blacks in general, and also many of the reds, violets or blue tones show no fluorescence, but a number of pink, orange and yellow dyestuffs are fluorescent on most materials. We may consider a few of the brightly fluorescing dyestuffs very suitably by classifying them according to the textile for which they are used.

Dyed Cotton

Basic Colours can be dyed on a tannin/antimony mordant or on an artificial mordant of the Taninol type ; when the latter is used the dyeings appear much duller in ultra-violet light then when tannin/antimony mordant is employed. By this means Rhodamine BS and especially Auramine OS dyed on Taninol mordant can readily be distinguished from dyeings carried out on goods mordanted with

[1] Hirst, *J. Text. Inst.*, 1937, **18**, 369.

tannin/tartar emetic. The fluorescence shown by any of the basic colours on mordanted cotton is duller and less intense than when " dyed " without a mordant on this substance or when dyed on wool and silk. The loading of the molecule of the dyestuff with the molecule of the mordant obviously decreases the excitability of the whole complex.

Methyl Violet 2 BS and 10 BS, Magenta PS and the various Methylene Blues and Bismarck Browns are non-fluorescent on either mordant.

Substantive or "Direct" Colours. Practically all of the substantive class of dyestuffs show little or no fluorescence, even many of the bright yellows appearing a dark reddish brown. Chlorazol Yellow 2GS, Primuline AS and the Primuline derivative Dianil Yellow 3GN show a yellow and a green fluorescence respectively, which is about as strong as that of Auramine OS and therefore of a high order.

Primuline AS dyed on cotton and developed shows the following behaviour : (*a*) alone, brilliant fluorescence, greener than the shade in daylight ; (*b*) hypochlorite—yellow ; (*c*) phenol—gold ; (*d*) resorcine—practically nil ; (*e*) β-naphthol—red ; (*f*) metaphenylenediamine—nil.

The fluorescence shown by a dyestuff is generally less brilliant on cotton than on wool or silk, but on the lustrous threads of viscose the intensity is greatly increased. Chlorazol Pink YS and other derivatives of dehydrothiotoluidine containing a thiazol ring, *e.g.* Diamine Rose BD and Thiazin Red GXX, show fairly strong reddish shades of fluorescence in medium and deep dyeings, but in very weak dyeings the fluorescent colour tends towards white at the same time being much less intense. Congo Red and Oxamin Red BN are two other dyestuffs showing red shades.

Chlorazol Fast Yellow BNS and FGS, Thioflavin S and its derivative Oxamin Yellow 3G show strong yellow fluorescence colours under the lamp. A mixture of Thioflavin S with certain direct colours of the Soluble Blue type appears green, a similar fluorescence being shown by the sulphur colour Immedial Yellow GG.

Chrysophenine GS, Chlorazol Fast Orange GS (golden brown), Chlorazol Fast Red 10BS (blue violet), Chlorazol Fast Scarlet 4BS (red), Congo Red WS (brilliant red), Benzopurpurine 4BS and 10BS (bright red), Chlorazol Violet RS (bright red), Chlorazol Sky Blue FFS (bright red violet) are other dyestuffs having marked fluorescence colours under the lamp on cotton.

The majority of the blacks, browns, blues and greens appear either dark under the lamp or very similar to the colour in daylight, but with the red, yellow and violet dyestuffs specific differences are often shown, sometimes so specific as to suggest the use of the lamp for their identification, always assuming, of course, that a very wide

range of dyestuffs is available for comparison. After-treatment with metals salts and formaldehyde dulls the fluorescence, and this must be allowed for when examining a colour which can be so treated, although the differences are not such that detection could be based thereon.

Vat Dyestuffs. The examination of vat dyestuffs in solution has already been mentioned, and on cotton fabric Caledon Yellow 3GS and 5GS show strong fluorescence colours. Anthraflavone G and RR fluoresce bright yellow and Hydron Yellow G (orange) is very strongly fluorescent. Anthra Scarlet GG (bright red), Anthra Brilliant-Green 5G (yellow) are other vat dyestuffs showing fluorescence on cotton. Among the reds to show fluorescence may be mentioned Durindone Scarlet YS (salmon red), Durindone Pink FFS and FBS (blue reds) and Durindone Red BS (reddish purple). As Durindone Orange RS has a yellowish red fluorescence it will be seen that the fluorescence colours of the above dyestuffs change in the same direction as the colour in daylight. Mixtures of Durindone Orange RS and Pink FFS or FBS give intermediate shades of red.

Azoic Dyestuffs. These dyestuffs appear dark purple under the lamp with the exception of Brenthol AS combinations with Fast Scarlet G, GG and RC bases which produce red tones. Breaking down the dyestuff by spotting the patterns with concentrated nitric acid, stannous chloride and hydrochloric acid, or sodium hydrosulphite and ammonia gives no characteristic fluorescence colours which could be of use in identification of the combination.

Wool and Silk

These two fibres can be considered together, as dyestuffs which fluoresce on one material invariably fluoresce on the other with, perhaps, a very slight change in the intensity and colour of the fluorescence.

Basic Colours. The Rhodamines show the strongest fluorescence while Auramine OS, Acridine Orange RS and Acronol Yellow TS also give brilliant fluorescence effects. Basic dyestuffs showing a less intense fluorescence than the above include Safranine TS, Chrysoidine YS, Magenta PS, Methyl Violet 2BS and 10BS, Methyl Violet RS and Victoria Blue BS and RS. The fluorescence colours are brightest when the dyeings are in the region of 0·2 to 0·5 per cent.

Direct Colours. Many direct colours show some fluorescence in weak shades, but the most outstanding from the point of view of intensity on silk are Chlorazol Corinth GWS (bright red), Chlorazol Pink YS (yellow red), Chlorazol Violet RS (bright bluish red), Chlorazol Sky Blue FFS and Chlorazol Blue GS (sky blue), Chlorazol Blue RWS

(blue-violet), Chlorazol Blue 2RS and Chlorazol Black JHS (bluish reds). Some of the above changes, which are best observed on dyeings of about 0·4 per cent. strength, are quite striking, the last-named being particularly so, as the colours in daylight are rather dull reddish blues, but under the lamp they appear as fairly bright bluish reds. In heavy shades the fluorescence colours are much less marked except in the red shades.

After-treatment of Chlorazol Sky Blue FFS, Chlorazol Blue GS and Chlorazol Blue RWS with copper sulphate decreases the fluorescence, but not sufficiently to allow the use of the method for the detection of " coppered " dyeings. As the strength of the dyeings of the above dyestuffs are increased from 0·4 per cent. to heavier shades, say, 2·0 to 3·0 per cent., the fluorescence intensity decreases, and at 3 per cent. only the yellows and reds show any notable fluorescence, thus conforming more or less to the general rule noted above.

Vat Dyestuffs. The most noteworthy of the vat dyestuffs showing fluorescence on silk are Indanthrene Yellow GK, Caledon Yellow 5GS (deep yellow), Caledon Red X5BS (bright pink), Caledon Red Violet 2RNS (bluish purple), Caledon Brilliant Purple 4RS (violet), Caledon Brilliant Violet RS (violet), Caledon Blue GCS, RCS and Brilliant Blue 3GS pastes (sky blue in light shades). The three blues in 20 per cent. shades appear very dark blue and allow of no differentiation, neither can any be made between the two violets mentioned and which appear deep violet. Caledon Jade Green brands of dyestuff fluoresce in pale shades, but again in heavy shades they appear black. Most of the reds and oranges in the Durindone range of dyestuffs show fluorescence and thus conform to the general rule (p. 808).

Acid Dyestuffs. On wool practically all the yellow dyestuffs with the exception of Tartrazine NS and Quinoline Yellow AS appear a deep greenish or dirty olive brown colour, and a number of the red shades of colour, even in 1 per cent. shades, appear almost black, exceptions being the Alizarine Rubinols, especially 5G and 3G which appear more yellowish in ultra-violet light than in daylight.

Many of the reds on wool show some fluorescence and appear lighter under the lamp than in daylight. The various halogenated phthalein derivatives such as Eosine YS, Phloxine BS, Erythrosin and Rose-bengal brands show strong fluorescence colours. Coomassie Milling Scarlet GS and 5BS also show fairly strong red fluorescence colours. Acid Magenta AS and Coomassie Violet 2RS, which are very similar in shade, can be distinguished from each other as the former gives a bluish red and the latter a bright scarlet red fluorescence, the latter being more intense than the former when dyed on silk. Coomassie Violet RS on wool shows a violet fluorescence in fairly

heavy shades and is the brightest on silk among the blue-toned dyestuffs and to a lesser extent fluorescence is shown by Lissamine Violet 10BS and 6BNS; all the other violets, however, appear dark in heavy shades and slightly fluorescent in light shades (0·3 to 0·6 per cent.). The effects observed are of little value, however, for identification work. Coomassie Brilliant Blue FFS shows a bright blue in weak shades and a deep blue in heavy shades both of good intensity.

On silk Naphthalene Scarlet BS shows a much more marked fluorescence than any of the other reds in the acid range of dyestuffs; among the blue dyestuffs Disulphine Blue EGS and Alkali Blue 4BS show fairly good fluorescence effects, and among the greens Disulphine Green BS, Lissamine Green SFS and especially Naphthalene Green GS, show fluorescence tones of bluish green. These dyestuffs also show fluorescence on wool.

Mordant colours on wool and silk are generally dark, although, should they be applied without a mordant, fluorescence colours are shown by some. Coomassie Milling Scarlet 5BS shows a decreased fluorescence when dyed by the afterchrome process, but this is not so marked as in the case of Coomassie Milling Scarlet GS. Solochrome Red 6BS shows a violet fluorescence whether dyed by the chromate process or the chrome mordant process, and with the exception of Alizarine Orange AS (yellow red) and Alizarine Red AS (bright red) is the only dyestuff to show fluorescence of any note. The alizarine dyestuffs mentioned only fluoresce when dyed by the chromate method, and if the afterchrome method is used they remain inert, the difference being sufficiently marked to allow differentiation between the dyeing methods employed.

Acetate Rayon

Of the dyestuffs used to colour acetate silk the anthraquinone type contributes a number of dyestuffs showing fairly bright fluorescence colours. Dyestuffs of the azo type rarely, if ever, contribute members having any notable fluorescence, and even the yellows and reds of this type are dull and inert under the lamp, in many cases appearing black in heavy shades.

Of the anthraquinone type a number of dyestuffs of red to yellow shades show fluorescence: Duranol Orange CS (bright yellow), Duranol Orange GS (bright orange), Duranol Scarlet 2G, B, 3B and Duranol Red X3BS show brilliant tones of bright scarlet nearly equal in intensity to basic colours. Duranol Red 2BS shows a fine blood-red fluorescence, but Duranol Red GS and B show only a slight dull red fluorescence and can be differentiated from the other Duranol reds and scarlets, especially in heavy shades.

The anthraquinone brown dyestuffs show a brown fluorescence lighter in colour than their shade in daylight and are easily distinguished from azo browns.

Among the blues, violets and blacks only Duranol Violet 2RS shows a fluorescence. In light shades this colour appears a light violet, but as the shade is built up the tone reddens, until in 5 per cent. shades it appears blood red. The most intense fluorescence of the acetate silk dyestuffs is shown by Duranol Brilliant Yellow 6GS (brilliant greenish yellow), and is equal to the brightest basic colour fluorescence of the same shade.

The water-soluble types of azo dyestuff used on acetate rayon all appear very dark under the lamp. Basic colours show their characteristic fluorescence colours similar in shade to those obtained on wool.

To sum up the position with regard to dyed fabrics, the lamp may be of some assistance in identification only if previous work and experience has sufficiently narrowed the possibilities to a very few colours, one or two of which show characteristic behaviour. Uneven dyeing may be detected in some cases by using the lamp, even although the dyeing appears fairly even in daylight, and the use of different mordants with basic colours can be detected. The chief value of the lamp lies in its application to special problems confronting the colourist from time to time and for some special routine tests which may be evolved by him for use in his own works.

Sizing and Dressing Agents

For identification of different substances, *e.g.* in sizing and dressing agents, the lamp can be of value. Many substances show a fluorescence in the massive state, but in thin films show little or no fluorescence or sometimes an increased fluorescence. Starches and dextrines are fluorescent in the massive state, but the colour of the fluorescence does not assist in the identification of the starch or dextrine used in sizes. Q. Hirsch [1] has, however, shown that diastase preparations often have a brilliant and characteristic fluorescence which is useful in their identification.

Waxes show dull fluorescence in the massive state, but on the fibre the only two that can be detected when present in reasonably small quantities are paraffin and carnauba, especially the latter. [2] A 1·0 per cent. solution of paraffin wax in chloroform shows a dull blue fluorescence, while 1/1000 of fatty grey carnauba wax gives a brilliant violet blue colour. The different varieties of carnauba wax appear to

[1] *Rev. Gén. Teint. Imp. Blanch.*, 1926, **6**, 541.
[2] Radley, *Analyst*, 1932, **57**, 626.

give somewhat varying results, some appearing similar to paraffin wax: the fatty grey, however, gives the brightest result. If the solution is evaporated to dryness, and the residues examined under the lamp, it forms a useful check test on the results obtained with the solutions.

A number of metallic compounds present in a dressing may be detected by causing them to take part in a reaction which gives a fluorescent end-product, and this is a method of general application.

A 10 g. portion of the cloth may be extracted at the boil with 100 ml. water for ten minutes, the liquid decanted, and that retained in the cloth squeezed out into the main bulk of liquid; the whole is then evaporated to about 25 ml., any soluble starch or dextrin precipitated by the addition of 3 to 4 times the volume of 96 per cent. alcohol and the mixture filtered.[1]

Borates or boric acid may be detected by acidifying a portion of this extract with acetic acid, boiling and adding a few ml. of the liquor to a few ml. of a solution of cochineal buffered to *p*H 5·8 to 6·9 with phosphate buffer, when the presence of boric acid is shown by a brilliant yellowish orange glow under the lamp. It is important to note that Al and Mg ions alter the shade of the fluorescence and lead, iron, copper or chromium ions impede the rate of its appearance, although when boric acid is absent they give no reactions with the cochineal.[2] The test should be checked by the usual turmeric and the alcohol/sulphuric acid tests.

Zinc salts may be detected by making a portion of the extract slightly alkaline with caustic soda and then acid again with acetic acid and adding a few drops of this liquid to an alcoholic solution of 8-hydroxyquinoline, when a brilliant yellowish green fluorescence appears if zinc is present. Magnesium unfortunately also gives a golden yellow fluorescence with this test, but a *specific* test for zinc is obtained by using a solution of urobilin instead of 8-hydroxyquinoline, when a characteristic brilliant green fluorescence is given in the presence of zinc.

Aluminium salts are detected by adding a few drops of the extract to an alcoholic solution of tetrahydroxyflavonol (morin or old fustic) when a bright greenish yellow fluorescence is shown in the presence of minute amounts of aluminium. If a piece of cloth dressed to give a 16 per cent. increase in weight with a size containing 1 per cent. each of zinc, magnesium and aluminium chlorides is spotted with alcoholic solutions of the above reagents and examined both before and after the spots have dried, the characteristic fluorescence colours can be seen quite distinctly.

[1] Radley, *J. Soc. Dyers and Col.*, 1937, 376.

[2] Szebelledy and Gaal, *Z. anal. Chem.*, 1934, **98**, 255.

The writer has applied this method to the examination of the storage of grey cloth. Zinc chloride is used in warp sizing and at first is entirely on the warp, but if it is stored under damp conditions it is frequently found on warp and weft. As grey cloth often contains appreciable amounts of magnesium salts the urobilin test must be used. A cloth not quite saturated with an alcoholic solution of urobilin is pressed on to the cloth to be tested for one to two seconds and the test sample examined through a lens under the lamp. With a cloth recently produced and stored in a dry place the warp threads only will be seen to be bright green, but with mildewed cloths or those stored in a very damp atmosphere both warp and weft will be green. The solution may be dropped on to the cloth direct if the solvent is evaporated as quickly as possible after application, *e.g.* by laying the cloth on a hot plate before applying the solution or ironing immediately afterwards in order to minimize solution and diffusion of the zinc salts present.

To detect or confirm aluminium salts in the presence of magnesium and zinc salts and in the presence of salts, *e.g.* calcium salts or other compounds commonly occurring in sizes and dressings, the dyestuffs Solochrome Dark Blue BS, Solochrome Violet RS and Solochrome Red ERS have been used by the writer. In the presence of traces of aluminium salts in slightly acidic, aqueous/alcoholic solution they give brilliant orange red fluorescence colours.

The test may be carried out by gently ashing the substance and taking up the ash in dilute hydrochloric acid and almost neutralizing with caustic soda solution. 1 ml. of a 0·2 per cent. solution of Solochrome Violet RS is then added, and the liquid boiled, cooled, diluted with an equal volume of 95 per cent. alcohol and examined under the lamp, when a brilliant orange fluorescence is obtained in the presence of 1 part per million of aluminium in the solution. Zinc salts give a dull blood-red fluorescence, but this does not interfere with the test even when they are present in great preponderance, as the orange fluorescence given by aluminium is so brilliant and distinctive. Instead of Solochrome Violet RS, Solochrome Red ERS or Solochrome Dark Blue BS can be used.[1]

If desired a dressed fabric or a size may be taken and extracted with hot water without ashing the material first. The solution is filtered, made slightly acid with hydrochloric acid and the test repeated as described above. In many cases an aqueous alcoholic solution of the dyestuff applied directly to the fabric and examined while wet gives the brilliant orange fluorescence, and it is rare indeed that this latter method fails to detect aluminium if this is present.

Of weighting agents present the lamp gives very little information

[1] Radley, *Analyst*, 1938, **63**, 266.

of analytical value, as the fluorescence of pigment whites often depends on the method of manufacture and the impurities present.

J. Grant, however, has been able to distinguish good china clay (weak violet) from mineral white (bright violet), talc (weak blue grey), blanc fixe (strong blue violet), and chalk (brighter blue). Titania of various grades could not be distinguished from china clay. Although the lamp in this case does not offer a great deal of assistance for actual identification in dressings, it is useful for checking deliveries of loading agents, and in one case it was useful in detecting tinting agents added to improve the colour.

Talc in a dressing can be detected by ashing a 2 g. portion of the dressing or finished cloth, extracting the ash with hot water, treating the residue with dilute hydrochloric acid, and washing with hot water to get rid of soluble salts and then taking it to dryness with conc. hydrochloric acid. The residue is taken up in a little water and tested with the alcoholic solution of 8-hydroxyquinoline sulphate to show the presence of magnesium.

A similar treatment, but using an alcoholic solution of morin extract or preferably using Solochrome Violet RS to detect the presence of aluminium, will show the presence of kaolin or china clay.

Urea formaldehyde resins fluoresce, but phenol formaldehyde resins do not.[1] Phthalic anhydride resins may be extracted with a solvent, which is driven off by heat, and treated on the water-bath with a few crystals of resorcinol and a few drops of conc. sulphuric acid, or heated to 130° for five minutes. The mass is diluted and made alkaline with caustic soda solution when an intense fluorescence is obtained from resins of this type.

Albumen shows a very bright bluish white fluorescence, and L. Mallet[2] has made the interesting observation that certain hypochlorites in solution when added to albumen cause it to emit ultra-violet light.

Casein shows quite a strong bluish white fluorescence, and it should be possible to apply the Voges-Proskauer reaction which was used by A. Harden and D. Norris[3] to detect protein material. For this purpose the material should be shaken with a 10 per cent. solution of caustic soda and 1 drop of 1 per cent. diacetyl solution added. In the presence of traces of protein matter a green fluorescence is obtained.

Gum arabic gives a bluish fluorescence but not nearly as strong as that shown by albumen, while gelatine also gives a bluish white fluorescence. Gum tragacanth is not readily detectable, as on textiles it has only a weak whitish fluorescence which cannot easily be seen.

Well-known wetting agents based on naphthalene sulphonic acids

[1] Kostka, *Chem.-Ztg.*, 1929, **53**, 117, 138.
[2] *Compt. rend.*, 1927, **185**, 352.
[3] *J. Physiol.*, 1911, **42**, 332.

or their salts and sulphoricinoleates show strong fluorescence colours in the mass. A stain made by 1 per cent. solution of a wetting agent of one of the above types on a white material shows a blue fluorescence under the lamp.

Nopitsch states that even after boiling and bleaching, traces of these wetting agents may still frequently be seen. The naphthalene sulphonic acids or their salts give violet to blue-rose fluorescence colours, more intense than the sulphoricinoleates and their salts, and when spotted on to fabrics generally show a brighter outer edge or halo which is absent in spots made by sulphoricinoleates. The latter, which fluoresce in yellowish to bluish white shades when spotted on fabric, do, however, show a halo sometimes when applied with a fat solvent as a miscible oil.

THE DETECTION OF FAULTS

Faults may be present in the raw materials used in a process or introduced during a process itself. Even after the article is finished it may become damaged by light, water, gas fumes, or contamination. Uneven dyeing by certain dyestuffs may readily be detected by visual examination, and under the lamp such differences are sometimes enhanced when the dyestuff is fluorescent, especially on artificial silk, natural silk and wool. Uneven dyeing caused by contamination of the cloth with mineral oil may be detected by the very strong fluorescence of the oil, especially in the light shades. In heavy shades, such as browns, blues and blacks, when very little fluorescence is observed, it is best to lay the uneven patch on a piece of clean cloth and pour a little of a non-fluorescent solvent, such as petroleum ether or chloroform, through the patch and to examine an underlying piece of cloth, when oil stains are readily detected. Such oil stains are plainly visible under the lamp if the colour is stripped, using as gentle a process as possible, having regard to the particular dyestuff employed.

Damage by bleach spots on cotton piece is readily detectable by the variation in fluorescence at such points. Sometimes dirty marks appear on cloth which may be due to its rubbing against a dirty and oily piece of machinery. Frequently such spots are so heavily charged with dirt that the fluorescence of the oil does not show through and then spotting with a non-fluorescent oil solvent is of great assistance, as the oil spreads out with the solvent and fluoresces brightly. Single strands, showing a bright fluorescence, sometimes indicate that the thread has been contaminated in the weaving, but patches of bright blue in which all the threads fluoresce, tend to show that the cloth has been contaminated with oil spots after weaving. Saturated hydrocarbons generally show no fluorescence, while unsaturated fatty acids and

resinous oils generally show a bright blue or violet and green fluorescence respectively, which change on exposure to light, thus giving some indication of the time since the contamination took place. Saturated fatty acids often show a white or yellowish white fluorescence and oxidized fatty acids a yellowish brown or no fluorescence. Vegetable and animal oils generally exhibit a pale yellowish fluorescence when fresh, but on ageing an intense yellow fluorescence. Fatty oils from vegetable sources are sometimes contaminated with chlorophyll which gives a red fluorescence which may become predominant in oils containing much of this compound. If present in oleic acid it can mask the blue fluorescence of the latter.

In actual practice, the oils used are generally mixed fatty acids or glycerides, so that it is preferable to record descriptions of the appearance of oils of known origin when examined in ultra-violet light. Traces of fatty oils which have oxidized are readily detected on wool by their yellow or brownish appearance.

Unsaturated hydrocarbons which have oxidized in air on wool show diminished fluorescence colour. In bulk, distilled oleine gives a clear violet fluorescence, but spotted on the cloth some samples show a fairly bright white fluorescence. Saponified oleine in bulk gives a buff fluorescence, the browning of the colour probably being due to an increase in the content of oxidized fatty acids. If oleic acid is oxidized to dihydroxystearic acid by means of alkaline permanganate the product is non-reactive under the lamp. Samples of oleic acid can vary greatly in their reaction under the lamp, some pure samples showing no fluorescence, redistilled samples appearing violet. One of the chief uses of the lamp here is to check delivered material against a sample of an oil ordered.

Irregular dyeing of wool may be due to stains brought about by mineral or fatty oils. On exposure to light the blue fluorescence of the former changes to white with a yellowish tinge and a yellow substance is precipitated from the oil ; oleic acid and vegetable oils show a more marked change on exposure than the above, and after seventy-two days' exposure to a carbon arc the fluorescence entirely disappears. After the oxidation in light and air has taken place the mineral oil type has conferred an increased affinity for dyestuffs on the wool whereas the oxidized vegetable oils or oleines act to some extent as resists.

To keep a record of the fluorescence colour of an oil, H. R. Hirst compared the oil with aqueous solutions of quinine sulphate which shows a brilliant blue fluorescence and Indigosol O showing a violet fluorescence, or mixtures of the two. If the fluorescence of the oil is too intense for comparison with the aqueous standard a known amount (10 ml.) should be diluted with petroleum ether (90 ml.) until the sample can be matched in colour and intensity with the aqueous

solutions. The dilution of the sample and the ratio of the two standard aqueous solutions in the matching liquid can then be recorded and reproduced at will.[1]

If at any time the determination of the amount of oil present in a cloth is necessary the method introduced by G. Blaser and Girsberger [2] can be used. A piece of cotton material 4×8 ins. is taken and immersed in a solution of 4 g. of machine oil in 20 ml. benzene, drained, dried and weighed. The increase in weight is due to the oil in the cloth and can be calculated from the amount of solution taken up by the cloth. Other solutions are made containing decreasing amounts of oil and cloth pieces immersed, dried and kept as standards. A strip of the fabric to be examined is laid on a black velvet and compared under the lamp with the standard strips. When the standard which it most closely matches is found, the amount of oil per square inch of the sample can be calculated.

In a recent printing process [3] highly fluorescent inert substances are added to the print pastes and an ultra-violet lamp is fixed in front of the printed fabric. It is claimed that scumming and snaps, etc., can readily be detected in this manner, and that this process is especially applicable to dyestuffs which give colourless printing pastes such as certain Indigosols and Soledons, Rapid Fast Colours and discharges.

Light damage in silk can be followed by the change in the colour of the fluorescence, and if degummed silk damaged by light is examined under the lamp it no longer appears bluish or white but exhibits the yellow tone that is shown by the raw silk, this change, according to A. Castiglioni,[4] being due to the action of sulphur acids on traces of cholesterol present.

Plant fibres, *e.g.* cotton, on prolonged exposure to light gradually assume a dark violet fluorescence which deepens progressively with continued exposure to light.

The marking off of dyestuffs on acetate silk can often be detected under the lamp, but usually such marking off is quite apparent visually. Cases of washing off of vat dyestuffs on cotton fabrics have been detectable by their fluorescence, when not visible in the normal way. Some moulds are fluorescent and can therefore be readily detected with the lamp.

Stains. It is sometimes desirable for those who are connected with the dry-cleaning and dyeing of already used apparel to be able to detect and distinguish between stains, and a few observations may be of interest.

[1] *J. Soc. Dyers and Col.*, 1931, **47**, 347; (1932), **48**, 90; (1934), **50**, 211.
[2] *Mell. Text. J.*, 1929, **10**, 963.
[3] *Textilber.*. Eng, Ed., 1937, **28**, 117.
[4] *Chim. e. Ind.*, 1935, **17**, 82.

Oil stains have already been mentioned. Paint stains may show practically no fluorescence or may appear a dirty purplish brown. The application of a few drops of solvent to such spots will give a ring of bright fluorescing substance, often yellow or greenish yellow in colour, while the pigment, usually non-fluorescent, is left in the centre. Dirty varnish stains behave similarly and give greenish yellow rings on spotting with solvents, and very brilliant stains are obtained in this way from tar or bitumen. Grease stains may be due to butter or other edible fats. The examination of the solutions obtained by extracting such a stain with petroleum ether will give information as to whether it is butter—this being the only one that shows a faint yellow fluorescence, the other edible fats in common use showing blue tones. Tea stains do not fluoresce, but coffee stains show a brilliant blue which is greatly increased in intensity if it has been sweetened with sugar.

Blood stains appear black under the lamp, while semen stains are a brilliant blue-white, and urine stains appear a little yellower and weaker than seminal stains. In criminological work blood stains are differentiated from iron stains by dissolving a thread or two of the stained material in conc. sulphuric acid, diluting with water, and making alkaline with ammonia when a brilliant carmine red fluorescence in ultra-violet light is obtained in the presence of blood. Spots on garments could not be treated with conc. sulphuric acid, but as 0·0002 ml. of blood in 5 ml. of water can be detected, sufficient can often be extracted with cold water to give the test.

Chlorophyll stains are differentiated from other green stains by the blood-red fluorescence given in the presence of solvents for chlorophyll. Iron gall ink stains appear dark after ageing and dark blue with a lighter blue outer ring when freshly made. Red ink based on eosine is highly fluorescent, but other coloured inks are comparatively dull in appearance under the lamp, especially if made on a coloured material. The colour of the material investigated will naturally affect the results as mentioned previously in connection with mineral oil stains.

XI. TEXTILE AUXILIARIES

By J. R. Hannay, F.I.C.

The problem of devising testing and valuation methods for the constantly increasing number of materials which come on the market under the general description of "textile auxiliaries" has produced a voluminous literature, but so far without the emergence of any generally accepted methods.

The variety of types of these materials is one reason for this, and the multiplicity of purposes they are intended to serve is another.

Haller and Landolt have classified these materials under the following headings :—

1. (*a*) Soaps, including resin soaps.
   (*b*) Mixtures of soaps and fat solvents.
2. (*a*) Sulphoricinoleates.
   (*b*) Mixtures of the latter with fat solvents.
3. (*a*) Alkylated naphthalene sulphonic acids.
   (*b*) Mixtures of the latter with fat solvents.
4. Miscellaneous bodies including :—
   (*a*) Pyridine derivatives.
   (*b*) Cholic acid derivatives.
   (*c*) Cresols and mixtures with fat solvents.
   (*d*) Derivatives of ethylenediamine.
   (*e*) Mixtures of members of this group.

To their list must be added :—

5. Derivatives of the higher fatty alcohols.
6. Protein degradation products.
7. Organic oxidizing agents possessing also wetting or detergent properties or both.

Such materials are marketed to serve as—

(*a*) Detergents.
(*b*) Wetting-out agents.
(*c*) Dispersing agents.
(*d*) Emulsifiers.
(*e*) Grease solvents.
(*f*) Protective colloids.
(*g*) Anti-foaming agents.
(*h*) Water-softeners.
(*j*) Finishing materials.

In many instances it is claimed that one material will serve several of these purposes.

A. GENERAL TESTS

In the older types of detergents and finishing agents it was usually sufficient to determine the content of free and combined alkali, and of free and combined fatty acid in order to obtain a fair idea of the value of any particular sample, but not only is the composition of many of the new materials known only to the manufacturers, but even when the chemical nature of a material is common knowledge the mere determination of the percentage of the effective chemical present will often be of only slight value in determining the practical commercial value of a product. For example, it does not help one to determine which of two products is most suitable as a wetting-out agent to know that one contains 60 per cent. of a sulphonated fatty alcohol while the other contains 50 per cent. of a pyridinium compound. Such knowledge is only useful in comparing samples containing varying percentages of similar constituents, or in comparing varying percentages

of differing composition when the relative value of the different compounds for the required purpose has already been thoroughly established.

The methods in use for the valuation of such bodies are consequently largely empirical, and only in a few instances are fundamental chemical or physical measurements employed. These empirical methods, intelligently employed, are capable of giving a practical comparison of the usefulness of widely different chemical individuals for particular applications. In using such tests it is always necessary to bear in mind that a test which has shown a sample to be the most suitable for one purpose does not necessarily prove its superiority for other purposes for which its use may be recommended.

Wetting-out Agents

From time to time, and by different workers, the determination of the drop number, by means of a Donnan pipette using an aqueous solution of the reagent to be tested and petroleum ether or kerosene oil, has been used as a measure of wetting efficiency. This is a measure of the interfacial tension of the two liquids. The larger the drop number the less the interfacial tension, and, it is argued, the greater the wetting power. Several workers have, however, pointed out that while drop numbers so determined give a general indication of the usefulness of any product as a wetting-out agent, there is no direct relationship between such numbers and the relative ability of a variety of samples to wet a given surface.[1, 2, 3] Yet this is one determination which, in conjunction with other tests, is fitted to give useful information to experienced workers.

The more empirical methods which have been devised for the most part depend either on observation of the time taken for a standard material to sink in a solution of the sample, or in measuring the amount of a solution of the sample taken up by a standard material under controlled conditions. In carrying out such tests care should be taken to make the conditions approximate as closely as possible to those under which the materials are to be employed in technical practice. Acidity, alkalinity, or salinity should be the same as that of the working baths, and where the material is intended for use in a bath of gradually rising temperature it is advisable to make tests at the initial and finishing temperatures as well as at an intermediate temperature.

Sinking Methods.—G. Bernardy [4] carefully introduces a skein of unbleached yarn, 4 cm. long and 3 mm. thick, into 100 ml. of a solution of the reagent under test. The time required to sink in the

[1] Auerbach, *Textilber.*, 1926, 7, 681-685.
[2] Auerbach and Kind, *Textilber.*, 1926, 7, 775-780.
[3] Rath, *J. Soc. Dyers and Col.*, 1928, **44**, 41-45.
[4] Bernardy, *Monatsschr. Textilind.*, 1926, 41, 18-20.

solution at a given temperature is noted, and gives a measure of the wetting power of the sample relative to that of any other sample tested under similar conditions. At least five tests should be made and the average time adopted as the test figure.

J. Auerbach [1] employed a piece of raw wool measuring 16 sq. cm., and noted the time required for penetration with a stop-watch. In later experiments in collaboration with W. Kind [2] he also used woollen yarn in the form of standard cross-wound reels in the same manner.

E. J. Rath [3] has recommended the use of a round piece of cloth of standard size made from hard-twisted, unbleached cotton yarn, to which a small weight is attached. This is placed carefully on the surface of the solution to be tested, which is contained in a glass cylinder, and allowed to sink into the liquor immediately, whereupon it begins to swing. When wetting-out is completed swinging ceases and the cloth sinks to the bottom of the cylinder. The time required for the cloth to sink affords a measure of the wetting efficiency of the sample.

Morgan, Pratt and Pettet [4] used the following technique for evaluating wetting-out agents intended for use in mercerizing. The method is quite capable of adaptation for use under any conditions :—

15 yards of unbleached 2/40's Sakel yarn are wound into skein form over a flat stick 27 ins. long, so as to give 10 turns of 1·5 yards each. The skein is folded thrice, giving successively smaller bands of yarn, and the final small circle twisted to form a bow, which is tied round the middle and flattened by hand pressure.

The test solution is made by adding 1 volume of the reagent to be tested to 100 volumes aqueous caustic soda containing 26 g. NaOH in 100 g. solution, and the liquid well stirred to ensure homogeneity. The bow is placed gently on the surface of the liquid and the time for complete wetting-out is noted. Three bows are thus observed and the mean time calculated.

Centrifuge Methods.—J. G. Evans [5] has described a modification of a method originally devised by Herbig [6] and described by him in *Die Öle und Fette in der Textilindustrie*. The method depends upon the statement of wetting power as percentage solution absorbed on a given fibre when immersed in a solution of the wetting agent. In Herbig's original reference cotton yarn was weighed, dipped in a solution of the wetting agent for five seconds, and the superfluous liquor removed in a hand centrifuge. Evans describes an apparatus designed to give greater exactitude to the method. It consists of a

[1] Auerbach, *Textilber.*, 1926, **7**, 681-685.
[2] Auerbach and Kind, *Textilber.*, 1926, **7**, 775-780.
[3] Rath, *J. Soc. Dyers and Col.*, 1928, **44**, 41-45.
[4] Morgan, Pratt and Pettet, *J. Soc. Dyers and Col.*, 1933, **49**, 125.
[5] Evans, *J. Soc. Dyers and Col.*, 1935, **51**, 233.
[6] *Cf.* Dhingra, Uppal and Venkataraman, *J. Soc. Dyers and Col.*, 1937, **53**, 91, who suggest a modified Herbig apparatus (made by Messrs Gallenkamp).

long glass cylinder of about 900 ml. capacity mounted in a sliding mechanism, capable of being moved up and down vertically by means of a treadle arrangement. Above the cylinder is a metal L-shaped arm mounted on an axis geared at the other end to a small electric motor. From this arm the textile material, on which tests are to be carried out, can be suspended. The cylinder containing the wetting agent can be thrust upwards rapidly by the sliding arrangement, so that the material is immersed completely.

After a given interval the cylinder can be dropped, and the motor set in motion so that the arm revolves and the wet material is centrifuged. In order to control the extent of centrifuging there is a de-clutching arrangement on the axis, and this can be set to give a definite number of revolutions before coming into action and stopping the machine.

The method of procedure is as follows :—

Grey Egyptian cotton yarn, free from size, is wound to form small hanks of approximately 0·5 g. each. In any given test the hanks should all be wound from the same cone to a length of about 12 cm., and allowed to condition in the room in which the tests are to be made for some time before use.

Five of these hanks are then weighed in a stoppered weighing bottle. One of the hanks is then suspended from the arm of the apparatus and a small weight attached to keep the yarn taut during immersion in the wetting solution. The cylinder should always be filled to the same level and any froth removed before commencing a test. After immersion for fifteen seconds the yarn is centrifuged (without the weight) for 100 revs. at 1000 r.p.m. and replaced in the weighing bottle. The other four hanks are treated in the same way. The increase in weight of the hanks expressed as a percentage on the original dry weight is the measure of the wetting power, and is termed the Herbig figure. By using five hanks in this way a mean of five determinations is obtained with only two weighings.

Lehner and Smith[1] have proposed another modification of the original Herbig method which does not appear to offer any advantages over the procedure just described, except that the apparatus is not quite so elaborate.

A skein of raw 40/2's cotton yarn, approximately 5 g. in weight, is weighed to the nearest centigram. The yarn is pulled tight several times in order to line up the strands, then doubled to form a loop of half the original length, and attached to an anchor. The skein is then cut open at the top with a pair of shears and struck on the palm of the hand eight or ten times in order to separate and free the individual strands. This preparation produces uniformity in the physical condition

[1] Lehner and Smith, *Ind. Eng. Chem.* (*Anal.*), 1933, 5, 376.

of the skeins, while the shearing of the yarn facilitates the rapid expulsion of adsorbed air by the solution as it penetrates the fibres. The skein and anchor are dropped into a cylinder containing a solution of the penetrating agent at a known concentration. The yarn is immersed in this solution for a time, measured on a stop-watch graduated to read to fifths of a second, and is then transferred to the slowly revolving basket of a centrifuge by pouring the entire contents of the cylinder into the basket. The centrifuge recommended is a hand machine with a gear ratio of 1 to 36 and a basket radius of 5·5 cm. Since the time of contact of the yarn with the liquid is an important factor in this test, care should be taken that the skein drops from the cylinder into the basket with a variation of only a few fifths of a second from the desired wetting-out time. Within one second after the transfer of the skein the speed of the slowly rotating basket is brought to approximately 2160 r.p.m., and the extraneous solution removed. The basket is revolved at this speed for the desired time, and then stopped rapidly by means of a braking force. The skein is removed, detached from the anchor, and weighed in a weighing bottle. The quantity of solution retained by the yarn is expressed in terms of a percentage of the initial weight of the skein. As a result of many trials a standard immersion time of fifteen seconds, and a standard centrifuging time of fifteen seconds is recommended. At least five determinations should be made and the results averaged. It is claimed that while individual tests may show some variation, the mean averages represent reasonably accurate evaluations of the quantity of solution retained by the fibres. The probable error in the mean average of a series was determined by the equation

$$\text{Probable error} = 0{\cdot}6745\sqrt{\frac{\Sigma a^2}{n(n-1)}}$$

where Σa^2 is the sum of the squares of the deviations of the single observations from the mean. It was found that the probable error in the mean average was in each case less than 1·5 per cent. It is claimed for this method that it gives a comprehensive evaluation and comparison of textile assistants. Evaluations made by this method give a direct measure of the most important factor in the penetration of textile fibres, *i.e.* a measure of the quantity of a solution absorbed by the fibre.

The amount of solution absorbed at the end of any time, at any desired concentration of wetting agent, can be determined regardless of the degree of saturation which the fibre has reached.

The centrifugal method makes possible a determination of the maximum absorption of liquid by a fibre in solutions of all textile assistants. Measurements may be made at any temperature with the assurance that the results obtained are comparable with those obtained

at any other temperature. The method is applicable to all types of textile fibres.

The technique involved in the use of the centrifugal method is readily acquired by anyone experienced in laboratory methods.

The time required for a test compares favourably with the sinking-time method. A series of five individual determinations required for the evaluation of a sample at a given concentration can be made in from fifteen to twenty minutes.

Dyeing Tests.—Wetting agents are often used as assistants in dyeing, and it is frequently assumed that the efficiency of an assistant as a wetting agent is a measure of its usefulness as an aid to the production of penetrated and level dyeings. But a material which will wet out a textile material instantly does not necessarily cause a dyestuff in the same bath to penetrate deeply and evenly into the fibre. It has been suggested that some measure of the usefulness of assistants for dyeing could be obtained by immersing a short length of tightly spun cotton rope, $\frac{3}{4}$ in. to 1 in. in diameter, in a solution of dyestuff containing an addition of assistant and observing the depth to which the colour has penetrated the rope. The technique of such a method does not seem to have been carefully worked out, but for certain purposes it could possibly be used to advantage. If, for instance, 2 to 3-in. lengths of cotton rope were immersed for a standard time in a solution of dyestuff and assistant, centrifuged as described in the methods above, the rope immediately cut across the middle with a sharp knife and the depth of colour penetration measured, it should be possible to make comparisons in this way between various textile assistants.

In using such a method one must bear in mind that results obtained with one dyestuff are not necessarily transferable to others. Tests should be made with each particular dyestuff to which the addition of an assistant is considered necessary.

Powney's Apparatus.—An attempt to apply more strictly scientific methods to the evaluation of wetting agents has been described by J. Powney.[1] The method depends on the changes which take place in the electrical resistance of a fabric membrane when it is being wetted by a solution on two sides.

The apparatus used (Fig. 139) consists of two identical sections, each having a glass reservoir of 250 ml. capacity attached to an ebonite collar. Steel-plate backing is used to strengthen the ebonite, and the glass to ebonite joints are made air- and water-tight by wide bore india-rubber tubing. Each section is fitted with a disc electrode fixed centrally just behind the opening in the flange plate. The two sections can be tightly clamped together by means of bolts and wing nuts, and the

[1] Powney, *Wetting and Detergency*, p. 185, Harvey, London, 1937.

apparatus is mounted so that it can be revolved about a central point and fixed in any desired position. In use the two reservoirs are filled to a convenient mark with the solution to be tested. The amount of solution used must be sufficient to cover completely the fabric membrane fixed between the two sections. The area of fabric penetrable by the test solution is sharply defined by the high pressure at the joint of the circular aperture. The electrical equipment consists of a stabilized mains-driven oscillator giving a constant source of 1000 cycle A.C., with a copper rectifier and galvanometer.

The electrodes of the wetting apparatus are connected to a special output circuit in the oscillator and the system calibrated in terms of the

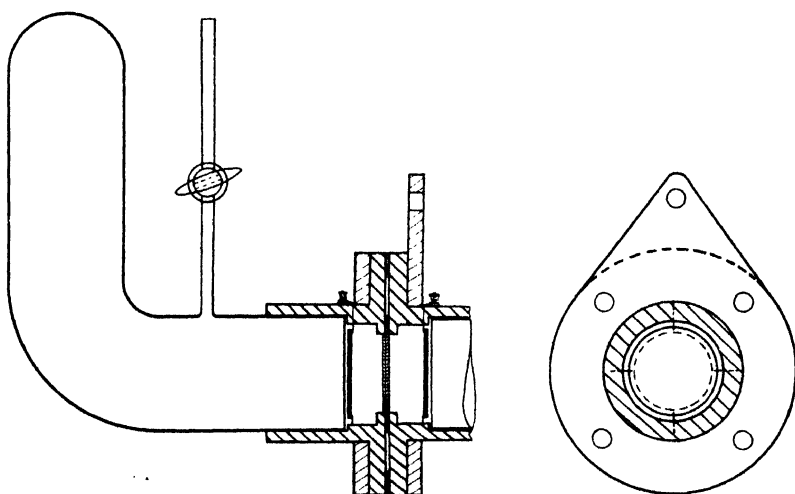



Fig. 139.

equivalent shunt resistance of the apparatus. The calibration covers a resistance range of 50 to 100,000 ohms in three stages.

The apparatus is inverted so that the solution covers both sides of the fabric membrane evenly, and the resistance between the electrodes is measured at convenient intervals until a steady value is obtained indicating complete penetration.

When penetration is extremely slow and it is not desired to record the whole course of the penetration, suction may be applied to one side of the apparatus, thus forcing the solution through the membrane to obtain complete saturation. The degree of penetration (P_t) after any time interval is calculated from the relationship :—

$$P_t = \frac{R}{R_t} \times 100$$

R_t is the resistance after time t, and R is the resistance at complete saturation. The use of this formula involves the assumption that the

mean specific conductivity of the solution within the fabric does not differ materially from that in the bulk.

The choice of a fabric for use in such an apparatus requires care. The material should be as uniform in structure as possible, and of such a character that reasonable time is required for penetration. Thoroughly scoured cotton fabrics are so rapidly penetrated that accurate measurements are impossible. Powney used a 5-ply fabric of partially scoured cotton containing 0·4 per cent. of residual fatty matter. The fabric membranes are all cut to the same size and conditioned at 70 per cent. R.H. before use. It is recommended that an average of at least three tests should be taken for each evaluation.

Resistance to Hard Water

The value of many textile assistants depends, at least partially, on the fact that they do not form precipitates with hard water ; and that, in conjunction with soaps and other fatty detergents or finishing agents, lime and magnesia soaps are kept in such a fine state of dispersion that they cease to be troublesome.

The effectiveness of various materials in this direction can be tested by two alternative direct chemical methods :—

(*a*) Either a chemically prepared standard hard water, or the natural water with which the materials under test are to be used can be employed.

To a given quantity of the hard water a measured amount of a solution of the sample under test is added. The mixture should be contained in a stoppered bottle or cylinder to admit of vigorous shaking. A standard solution of soap is run into the mixture from a burette until the solution shows a distinct and permanent milkiness. The greater the quantity of soap solution required the more efficient is the sample.

(*b*) Standard soap solution is added to the hard water until precipitation of the alkaline earth soaps is complete, *i.e.* until a lather persisting for one minute is obtained on shaking. A standard solution of the material under test is then run in from a burette until complete dispersion of the alkaline earth soaps is obtained. The smaller the amount of the sample required the more efficient it is.

When results are required to be comparable in tests done at long intervals it is advisable to prepare an artificial hard water which can always be exactly repeated. For experimental purposes a hard water prepared from Iceland spar is quite satisfactory, but for technical purposes a water containing a proportion of magnesium salts is often preferable.

Stability to Acids and Saline Solutions

Textile auxiliaries are frequently recommended for use in processes such as wool dyeing, carbonizing, or direct dyeing of cellulose fibres, which have to be carried out in acid or saline baths. Materials intended for such purposes should be tested under conditions approximating to those obtaining in practice. Additions of the auxiliary to acids of the kind and strength to be used in process should be made and the behaviour of the mixture noted over the range of temperatures to which it will be subjected.

Materials to be used as additions to baths for the direct dyeing of cellulosic fibres should be tested by boiling in solutions of sodium chloride, sulphate, phosphate and carbonate. When they are to be used in a standing bath the effect of prolonged heating should be noted. Materials intended for use with " salts " finishes should be tested by heating with strong solutions of magnesium sulphate and barium chloride.

Stability to Strong Caustic Alkalis

The advantages to be derived from a reagent which would enable caustic alkalis of mercerizing strength to wet-out grey cotton rapidly and evenly are so obvious that considerable attention has been given to the development of a class of auxiliaries for this special purpose. Many compounds which serve well in neutral, acid and saline media are quite useless in caustic solutions of mercerizing strength.

Many of the most successful auxiliaries for this purpose consist largely of crude cresols with or without the addition of hydrogenated hydrocarbons or phenols. " Mercerol " and " Inferol M " are examples of such bodies. " Shirlacrol " consists of the fraction of the tar acids from low temperature tar distilling at 210° to 270°. " Leophen M " is the sulphuric ester of an alcohol (boiling point, 120° to 160°) obtained as a by-product in the high pressure hydrogenation process for the manufacture of methyl alcohol.

Such auxiliaries should always be examined for stability by observing their behaviour when allowed to stand for forty-eight hours in caustic soda 55° Tw. at 15°.

The evaluation of mercerizing assistants is probably best carried out by one of the centrifugal methods described under " Wetting-out Agents," (p. 823), although the " sinking " method may also be used when other apparatus is not available.

It is always advisable to make these tests on a fresh mixing of caustic and auxiliary, and to repeat them at convenient intervals over forty-eight hours, using the same mixing. Comparison of the various results will afford valuable evidence regarding the stability of the sample under test.

Detergency

Many of the new auxiliaries are claimed to be good detergents or cleansing agents, and an efficiency many times greater than that of soap is claimed for some of them. Although there has been much investigation of the mechanism of detergency and a voluminous literature exits on the subject, up to the present no precise agreement on the relative importance of the various properties which a good detergent should possess has been reached, and consequently no standard methods of testing have been evolved.

It can, however, be definitely affirmed that as a result of work carried out in recent years we have a much clearer idea of what happens during the cleansing of a soiled fabric than was the case of a few years ago, and it appears to be fairly well established that good detergency is the cumulative effect of several properties which different cleansing materials possess in varying degrees and proportions.[1, 2, 3]

Among the most essential of these properties are (i) the power to lower the interfacial tension between water and the fabric; (ii) deflocculating or peptizing properties; (iii) protective colloid properties; and (iv) the power to retain the removed dirt in suspension. It is necessary to note that the properties mentioned under (ii), although similarly effective in a detergent, are not synonymous. E. J. Acheson [4] distinguishes between them in the following manner. Deflocculating power is a more general property than the power to cause peptization. One agent will usually deflocculate or disperse many diverse substances. In deflocculation mechanical action is necessary, but such mechanical action does *not* infer grinding. Peptization is a more particular quality. As a rule the power to effect peptization is specific between the reacting substances, *e.g.* oxalic acid will peptize Prussian blue but is without action on china clay.

These various properties of a good detergent are not easy to evaluate, and when they have been determined there exist, as yet, no reliable data to equate the exact amount of efficiency attributable to the separate properties; consequently for technical purposes some form of practical cleansing trial conducted under controlled conditions is usually relied on.

Such trials are not really difficult to devise, and details must often be dependent on the type of apparatus available. Details of some methods which have been used by various workers in this field will be found in the section dealing with Soaps (p. 839).

[1] Acheson, Alexander's *Colloid Chemistry*, 3, 548 *et seq.*
[2] Elledge, *ibid.*, 4, 635 *et seq.*
[3] Zacharias, *ibid.*, 4, 653 *et seq.*
[4] Acheson, *ibid.*, 3, 548 *et seq.*

A method devised by Baker [1] when investigating the detergent properties of sodium metasilicate may be found useful when there is a difficulty in obtaining a suitable standard fabric, or of finding means for the regular distribution of the standard " soil."

A series of test-tubes, 10 mm. diameter, are carefully cleaned and dried. About 1 ml. warm petroleum oil is then placed in the tubes while still hot and each tube rotated so as to distribute the oil evenly over the surface. The tube is immediately cooled and placed in a rack. Quantities of the solutions to be tested are put into the tubes and their effectiveness in removing the oil from the sides of the tubes and forming a distinct oily or emulsified layer on the top of the liquid is noted from time to time. The solution which effectively cleanses the sides of the tubes in the shortest time is reckoned the best detergent.

Protective Colloid Efficiency

Most workers in this field maintain that this property plays an important rôle in producing a good detergent, and the detergency tests already mentioned in some degree determine this property in conjunction with the other necessary properties.

This property has special importance when auxiliaries are recommended for special purposes, such as dyeing assistants designed to give more level dyeings either with difficult dyestuffs or on difficult textiles, or as emulsifying agents. Consequently, methods for the determination of this particular property are of some importance. Zsigmondy's " gold number " method is one of the earliest of these and is still employed by many workers.

The " gold number " is defined as the number of mg. of a protective colloid which just prevents the colour change in 10 ml. of a red gold sol. containing 0·0053 to 0·0056 per cent. Au, when 1 ml. of a 10 per cent. NaCl solution is added.

The red gold solution is prepared in the following manner :—

(i) 6 g. $AuCl_3HCl . 3H_2O$ dissolved in, and made up to 1 litre with freshly prepared doubly distilled water.

(ii) 1 litre $0·18/N K_2CO_3$ prepared with distilled water as (i).

(iii) 1 litre of 0·3 per cent. solution of formaldehyde also prepared with distilled water as (i).

Heat 240 ml. of the special distilled water and add 5 ml. solution (i) and 7 ml. solution (ii). Mix thoroughly and heat to 100°. Then 6 to 10 ml. of the formaldehyde solution is added with continuous stirring. A bright red solution should result.

The determination is usually carried out by placing 10 ml. of the gold solution in each of a series of ten test-tubes and adding amounts increasing by 0·1 ml.—from 0·1 ml. to 1 ml.—of a 1 to 5 per cent.

[1] Baker, *Ind. Eng. Chem.*, 1933, **25**, 1026.

solution of the material under test, according to effectiveness. These solutions should be mixed immediately and allowed to stand for three minutes. 1 ml. of 10 per cent. NaCl solution (approximately $2N$) is then added to each tube and the point at which the colour change takes place is noted. The conditions of the determination must be rigidly controlled if comparable results are to be obtained. In particular, all solutions should be made from twice distilled water, freshly prepared and, if possible, condensed through a silver worm.[1] Messrs Dhingra, Uppal and Venkataraman [2] in some recent work employed an inversion of this method which appears to offer a desirable simplification of the procedure. The solutions are prepared in the usual way, but the salt solution is run in from a burette and the amount just necessary to change the colour from red to blue is taken as a measure of protective efficiency, the larger the quantity required the more effective the protection. Bayrodt and Zacharias [3] prefer the " Congorubin number " originally devised by W. Ostwald. They maintain that although the general procedure is similar to the " gold number " method, it is simpler and more reliable.

A 0·01 per cent. solution of Congorubin in rigorously pure distilled water is prepared. To each of six test-tubes add 10 ml. of this solution and 1 ml. of the solution under test, mix thoroughly and allow to stand for five minutes. Various amounts of a 10 per cent. solution of NaCl are run in from a micro-burette. The amount is varied systematically so that each tube in the series receives an increment of 10 mg. NaCl over its predecessor. After standing for ten minutes some of the tubes usually show a definite colour change from red to lilac. For example, tubes 1, 2 and 3 may show no change, while 4, 5 and 6 are clearly over the end-point. Assuming 70 mg. NaCl had been added to tube 4 while tube 3 had received but 60 mg., the " Congorubin number " is defined as 60 for that particular sample.

" Blank " determinations, omitting any protective colloid, usually show a Congorubin number of 30 to 40 when reagents and technique are satisfactory.

CHEMICAL METHODS OF EVALUATION

Various methods for the chemical evaluation of certain types of textile auxiliaries have been devised, and some of the more serviceable are given below.

R. Hart [4] has worked out the following methods for the determination of sulphuric anhydride and salts in sulphonated fats which lose

[1] Zsigmondy and Schulz, *Z. anal. Chemie.*, 1901, **40**, 697.
[2] Dhingra, Uppal and Venkataraman, *J. Soc. Dyers and Col.*, 1937, **53**, 95.
[3] Zacharias, Alexander's *Colloid Chemistry*, **4**, 653 *et seq.*
[4] Hart, *Textile Manufacturer*, 1934, **60**, 337-339.

their combined SO_3 by boiling with mineral acids, and which do not contain ingredients that cannot be accurately titrated in aqueous solution with methyl orange as indicator.

(1) Alkalinity

Dissolve 10 g. of the sample in 100 ml. water in an Erlenmeyer flask, warming to effect solution if necessary. Add 30 g. sodium chloride, 25 ml. ether, 5 drops methyl orange and titrate the mixture with $N/2$ sulphuric acid. The flask should be stoppered frequently during the titration and the contents well shaken.

$$\text{Alkalinity} = \frac{\text{ml. } N/2 \text{ } H_2SO_4 \text{ used} \times \cdot 05}{\text{weight of sample}}$$

(2) Increase of Acidity on Boiling

Weigh 10 g. of the sample into an Erlenmeyer flask and boil for seventy-five minutes under an air condenser with excess of normal sulphuric acid, using glass beads to prevent bumping.

The amount of acid used should be that necessary to neutralize the alkalinity plus 25 ml. excess. The contents of the flask should be frequently agitated during boiling. After boiling, the condenser is washed into the flask with a few ml. distilled water, the condenser disconnected from the flask, and the contents cooled. Now add 30 g. sodium chloride, 25 ml. ether, 50 ml. distilled water and 5 drops methyl orange, and titrate the mixture with $N/1$ NaOH to the same end-point as the alkalinity titration. The flask should be stoppered frequently and the contents well shaken during the titration. A blank must be run simultaneously with the sample.

The increase in acidity is equal to the ml. NaOH required for the sample minus the ml. NaOH required for the blank multiplied by the normality of the caustic soda and divided by the weight of sample. The algebraic sum of the alkalinity and the increase in acidity equals the percentage of organically combined sulphuric anhydride

Gravimetric Method

(1) *In Absence of Ammonia.* Weigh 5 to 8 g. of the sample—according to concentration—into a 250 ml. pear-shaped separatory funnel containing 50 ml. of 25 per cent. sodium chloride solution, 5 drops methyl orange indicator, and 75 ml. ether. The mixture is shaken and neutralized with approximately normal sulphuric acid until the lower layer is distinctly pink (0·2 ml. excess).

If an emulsion forms, add alcohol—2 ml. at a time—until the

emulsion breaks, mixing gently after each addition. After settling, draw off the lower layer into another separation funnel and wash the ether layer with 20 ml. of 25 per cent. sodium chloride. The washings must be added to the water layer in the second funnel and the combined watery layers further extracted with two 20 ml. portions of ether. Add the ethereal extracts to the ether layer in the first funnel and carefully remove any water which may separate. Now shake the combined ether extracts with 10 ml. of the 25 per cent. sodium chloride solution for three to five minutes. After settling, remove the lower layer as completely as possible, warming with warm water or steam should the salt tend to crystallize. Cool the ether layer to 15°, scratching the inner wall of the funnel with a glass rod to induce crystallization of traces of salt, and finally filter into a dry Erlenmeyer flask. Wash the separation funnel, and crystals, if any, with three 10 ml. portions of ether, or until free from fatty matter.

Now immerse the ether solution in ice water for fifteen minutes, warm with a little stirring to 25° to 30° to bring back into solution any fat that may have separated, allow to settle and filter immediately into a dry 300 ml. flask. Wash the flask and filter paper with five 10 ml. portions of ether or until free from fatty matter. The filtered solution when chilled again to 0° and reheated to room temperature, should remain perfectly clear. Evaporate the ether solution until the volume is reduced to about 20 ml., and transfer it to a tared 50 ml. crucible (tall form). Immerse the crucible in a 100 ml. beaker of hot water until practically all the ether is evaporated. The flask should be rinsed with two 10 ml. and three 5 ml. portions of ether, or until all fat is transferred to the crucible, each addition of rinsing ether being made only after the previous rinsing has practically evaporated. Gently burn off the residue, and finally ignite to constant weight. To prevent creeping of oil and to hasten evaporation, the solution may be stirred with a glass rod. Before burning the oil the rod should be wiped clean with ashless filter paper, which should then be added to the crucible. To oxidize traces of carbon or sodium sulphide that might form, the ash is moistened with 30 per cent. hydrogen peroxide, and again carefully ignited to constant weight.

(2) *In Presence of Ammonia.* Dissolve 5 to 8 g. of the sample in 80 ml. distilled water in a 300 ml. flask, add 10 ml. normal caustic soda and boil the solution gently until a wet litmus paper held over the flask fails to indicate the disengagement of ammonia. Cool the solution and transfer it to a 300 ml. pear-shaped separation funnel, and add 35 g. of sodium chloride, or enough to make finally a 25 per cent. solution. Now add 5 drops methyl orange indicator and 75 ml. ether, and carry out the neutralization, extraction, etc., exactly as when no ammonia is present.

The weight of ash found by either of the foregoing methods divided by the weight of sample taken and multiplied by 100 equals the percentage of extracted ash in the sample. This, multiplied by 1·1267, equals the percentage of organically combined sulphuric anhydride. It is claimed that the volumetric and gravimetric methods give satisfactorily concordant results.

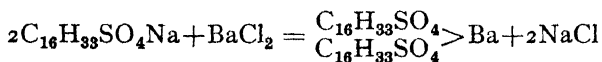
Organically combined Sulphuric Anhydride

J. R. Hannay [1] has published a scheme for the evaluation of materials of the type of the Gardinols, Adulcinols, Igepons, Lissapol, Sulphonated Ocenol and Lorol, Limsopon, Amoa-Falco, Gelsolan, etc. The quantities given may have to be varied with the concentration of the marketed product, but the method is generally applicable to all auxiliaries based on sulphonated aliphatic alcohols. About 10 g. of the product is dried in a water-oven at 100° for four hours, or until constant weight is attained, and the loss in weight calculated to percentage and stated as *loss at* 100°. This loss will include any volatile solvent which the sample may contain. The author doubts the value of such ingredients in scouring and finishing assistants for cellulosic materials as they will volatilize in the steam or on drying; he has never found the loss from such a source to exceed 3 per cent.

The dried sample is now dissolved in absolute alcohol and filtered through a dried tared filter paper. The insoluble residue, washed with several portions of warm alcohol, is dried and weighed. This residue includes all inorganic salts, proteins, or protein degradation products, and starches and gums, if any. If desired, chlorides, sulphates, phosphates and organic matter in the residue may be determined by the usual analytical methods. Evaporate the alcohol from the filtrate, dissolve the residue in water, and add an excess of barium chloride, which precipitates the barium salt of the aliphatic sulphonates. It is necessary to boil the solution, and to allow ample time for cooling and precipitation, a period of forty-eight hours being sometimes necessary; further addition of barium chloride to the filtrate is a good precaution to ensure that all the sulphonate is precipitated.

The barium salt is then filtered off, washed free from barium chloride, dried and weighed.

The reaction takes place according to the typical equation :—

$$2C_{16}H_{33}SO_4Na + BaCl_2 = \begin{matrix} C_{16}H_{33}SO_4 \\ C_{16}H_{33}SO_4 \end{matrix}\!\!>\!Ba + 2NaCl$$

and if the exact composition of the alcohol in the compound under examination is known the suitable calculation can be made. When the exact composition is unknown a sufficient indication of the

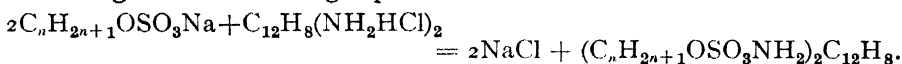
[1] Hannay, *J. Soc. Dyers and Col.*, 1934, 50, 275.

concentration of the material for technical purposes can be obtained by calculating to the C_{16} compound, as most of the assistants of this type contain either the C_{14}, C_{16}, or C_{18} alcohol.

The results obtained by this method are not strictly accurate, but the process is easily carried out in a works laboratory, accounts for 98 to 99 per cent. of the fatty alcohol sulphonates present, and gives a useful indication of the strength of the products examined. The results obtained can be usefully checked by the following further test.

Weigh out 5 to 10 g. of the sample into a 500 ml. flask, add 125 ml. distilled water and 125 ml. strong hydrochloric acid, and boil for two to three hours under a reflux condenser. The sulphuric acid ester group is hydrolyzed, and, after cooling, the fatty alcohol may be extracted with ether, or separated by wet filtration, and weighed. The alternative method is necessary, as difficultly separable emulsions are sometimes formed with ether. In the case of the Igepons there is considerable difficulty with this method. Hydrolysis occurs at the ester grouping, and after about thirty minutes refluxing oleic acid can be seen separating as a thin oil; further refluxing, however, causes the reaction to reverse, and finally the sulphonic acid complex may be salted out, separated and weighed. Agreement between results obtained by this method and those obtained by the barium chloride precipitation method is within 1 to 2 per cent.

Kertess[1] recommends the precipitation of sulphonated fatty alcohols with benzidine hydrochloride. The reaction takes place according to the following equation

$$2C_nH_{2n+1}OSO_3Na + C_{12}H_8(NH_2HCl)_2 = 2NaCl + (C_nH_{2n+1}OSO_3NH_2)_2C_{12}H_8.$$

The analytical details of the process, as worked out by Kling and Püschel,[2] are as follows :—

Preparation of Benzidine Hydrochloride Solution. An approximately $N/20$ solution of benzidine hydrochloride suitable for this method may be prepared by weighing out 4·603 g. pure benzidine, pasting with 50 ml. normal hydrochloric acid, and heating until the benzidine is dissolved. The solution should be filtered, if necessary, and made up to 1 litre. The reagent prepared in this way should have an acid reaction.

(I) Determination of Fatty Alcohol Sulphonates in Dilute Solutions.—Place 10 ml. $N/20$ benzidine solution in a 250 ml. beaker which has been thoroughly washed out with distilled water. Add 25 ml.—or in the case of very dilute solutions, containing less than 0·5 g. per litre, 50 or 100 ml.—of the solution under examination, shake the neutral or slightly acid solution well, and warm slightly.

[1] Kertess, *Textile Manufacturer*, 1934, **60**, 336.
[2] Kling and Püschel, *Textilber.*, 1934, **15**, 21.

If the solution to be tested has an alkaline reaction it must be neutralized before adding it to the benzidine solution. If it contains 2 g. or more per litre of fatty alcohol sulphonates, then 50 ml. *N*/20 benzidine solution must be used. The mixture should be vigorously shaken for long enough to allow the precipitate to agglomerate, and then allowed to stand for five or ten minutes. Filter through a qualitative filter,[1] wash the flask with three or four 20 ml. portions of distilled water, passing the washings through the filter. Any slight amount of precipitate adhering to the beaker may be neglected. Wash the precipitate on the filter at least three times with distilled water, and allow the wash water to drain off thoroughly. Any water remaining in the stem of the filter funnel should be removed by suction. The precipitate is now washed through the filter with warm alcohol until the filtrate bulks at least 40 ml., and at most 60 ml. It is a convenient plan to suspend the filter funnel over a graduated cylinder. The alcoholic solution is returned to the beaker in which the precipitation was carried out, 3 or 4 drops indicator solution (bromocresol purple, 0·04 per cent. in alcohol) added, and heated for five minutes on a water-bath kept just below boiling point.

While still hot the solution is titrated with *N*/100 KOH until the colour changes from yellow to blue.

Each time a new packet of filter papers (which always contain a certain amount of acid) is started, it is necessary to do a blank in order to determine the acidity of the filters. Pass 50 ml. hot alcohol through a filter paper and heat on a water-bath for five minutes, with the addition of 3 drops bromocresol purple (as above) and titrate with *N*/100 KOH until the colour changes to blue. This titration value must be deducted from all titrations made on samples filtered through papers from the same package. As a rule this will amount to 0·3 to 0·4 ml. *N*/100 KOH.

Calculation.

$$\frac{\text{ml. } N/100 \text{ KOH used} \times a}{\text{ml. fatty alcohol sulphonate sol. taken}} = \text{grams } C_nH_{2n+1}\,OSO_3Na/\text{litre.}$$

The factor *a*, which gives the number of mg. of the particular alcohol sulphonate being determined, equivalent to 1 ml. *N*/100 KOH, is for chemically pure salts.

$C_{12}H_{25}OSO_3Na$ . . . . . $a = 2·883$
$C_{14}H_{29}OSO_3Na$ . . . . . $a = 3·163$
$C_{16}H_{33}OSO_3Na$ . . . . . $a = 3·443$
$C_{18}H_{33}OSO_3Na$ . . . . . $a = 3·724$

Technical products usually contain several homologues of the series $C_nH_{2n+1}OSO_3Na$, besides various inorganic salts due to the

[1] Quantitative filters are apt to have greater acidity on account of their more vigorous purification, and are consequently less suitable.

method of manufacture, and hence such a straightforward calculation is impossible.

One can then only fix an empirical value for " *a* " by making a 1 g. per litre solution of the product, estimating the amount of *N*/100 KOH equivalent to 25 ml. of this solution, and calculating the value of " *a* " as follows :—

$$a = \frac{25}{\text{ml. } N/100 \text{ KOH used}}.$$

The factors found for a few well-known auxiliaries are given below :—

Gardinol C.A. powder .	.	$a = 10{\cdot}70$
,, W.A. conc. powder	.	$a = 7{\cdot}44$
,, W.A. ex. conc. powder	.	$a = 3{\cdot}80$
Brill. Avirol L. 142 conc.	.	$a = 5{\cdot}40$
,, ,, L. 168 conc.	.	$a = 13{\cdot}00$

(II) Determination of Inorganic Sulphates (Na_2SO_4) in the Presence of Fatty Alcohol Sulphonates.—It is possible to make this determination approximately by working on the residue left on the filter after dissolving out the benzidine sulphonate in (I) ; but as there is always some loss in washing with water it is advisable to take a fresh quantity.

Proceed exactly as under (I) up to the point at which the benzidine precipitate is thrown on the filter. At this point, instead of washing with water, as soon as all liquid has drained through the filter, wash the filter with 50 to 60 ml. hot alcohol. The filter paper and its contents are placed in a beaker, covered with 50 ml. distilled water, and heated just under the boil for ten minutes. Now add 5 to 6 drops phenol red solution (0·02 per cent. in alcohol) and titrate while still hot with *N*/100 KOH until the solution is red.

$$\frac{\text{ml. } N/100 \text{ KOH used} \times 0{\cdot}710}{\text{ml. fatty alcohol sulphonate sol. taken}} = \text{g. } Na_2SO_4\text{/litre.}$$

The accuracy of the method is illustrated by controlled analysis in which pure sodium alkyl sulphonates were determined with and without the addition of K_2SO_4.

Stock Solution 1 g. per litre.	*N*/100 KOH ml. used.	Conc. of Stock Sol.		Error per cent.
		By calculation grm./litre.	By titration grm./litre.	
$C_{14}H_{29}OSO_3Na$ (25 ml.)	7·75	1·00	0·98	−2
$C_{14}H_{29}OSO_3Na$ (25 ml.)+25 ml. K_2SO_4	7·80	1·00	0·99	−1
$C_{16}H_{33}OSO_3Na$ (25 ml.)	7·20	1·00	0·99	−1
$C_{16}H_{33}OSO_3Na$ (25 ml.)+25 ml. K_2SO_4	7·35	1·00	1·01	+1
$C_{18}H_{37}OSO_3Na$ (25 ml.)	6·60	1·00	0·98	−2
$C_{18}H_{37}OSO_3Na$ (25 ml.)+25 ml. K_2SO_4 (25 ml.)	6·70	1·00	1·00	0

It is claimed that with practice a determination may be made in about thirty minutes. The influence of impurities on the accuracy of the determination is not always easily detected, but it has been established that in the presence of soaps, sulphonated oils, and similar preparations, the results are not dependable. Such bodies all give more or less difficultly soluble compounds with benzidine, and consequently are always included to some degree in the alkyl-benzidine sulphonate precipitate.

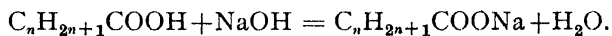
In technical analysis for textile purposes an endeavour should always be made to ascertain the nature of the substances other than alkyl sulphonates contained in the sample, and to make allowance for their influence on the determination.

B. SOAPS

Chemically, soaps are metallic salts of fatty or rosin acids, but technically and commercially the term soap is ordinarily confined to the potassium, sodium, and occasionally ammonium salts of fatty acids containing more than seven carbon atoms (and not more than twenty-two) with or without the addition of rosin acids.

Only the soaps of these three bases are appreciably soluble in water, and although other salts of fatty acids possess properties which render them valuable for a variety of purposes, they are usually referred to as "metallic soaps" or "plasters." Soaps may also be derived from the naphthenic acids obtained during the purification of certain crude petroleums. They are extracted from the crude oils by washing with alkali, and usually carry a considerable quantity of hydrocarbon oil in emulsion. The sodium salts are soluble in water and possess good cleansing properties, lathering freely. Unfortunately they have a most objectionable odour, and although careful purification can remove it temporarily, it invariably returns after a period. Consequently the attempts to utilize these otherwise excellent detergents has met with little commercial success.

Soaps may be formed by the direct reaction of an alkali hydroxide and a free fatty acid,

$$C_nH_{2n+1}COOH + NaOH = C_nH_{2n+1}COONa + H_2O.$$

If pure materials and molecular proportions are used, pure soaps are obtained. Such pure soaps are odourless, colourless, and neutral to phenolphthalein when concentrated. In dilute water solution such soaps give an alkaline reaction due to hydrolysis. It was formerly believed that the detergent properties of soap were almost entirely due to this hydrolysis, but the work of McBain and his collaborators has shown that even in weak solutions of oleates the hydrolysis was not equivalent to more than $N/300$ alkali, while for most solutions it

ranges from *N*/3000 to *N*/30,000. In laurates and palmitates the hydrolysis is even less than this.

Natural fats and oils of both animal and vegetable origin, such as tallow and palm oil, which form the usual sources of fatty acids for soap-making consist of mixed esters of various fatty acids with glycerol. The fatty acids found in greatest quantity in the fats used in the soap industry are stearic, palmitic and oleic acids. The liquid fats usually contain a high proportion of oleic acid, while the solid fats contain higher proportions of palmitic and stearic acids. In general the properties of a soap are indicated by the preponderating fatty acid it contains, and the nature of the alkali with which it is combined. Potash soaps are soft or pasty, while soda soaps are hard or firm. In addition to fatty acids and alkali, commercial soaps contain small proportions of impurities derived from raw materials and process liquors, water, and in many instances added fillers, some of which are intended to increase the efficiency of the soap, while others are purely diluents.

The method of valuation employed for a particular sample of soap is usually dependent on the purpose for which the soap is required. The efficiency of a soap as a detergent is almost wholly determined by the amount of combined fatty acid and alkali it contains, and soaps are commonly sold on a guarantee of a minimum fatty acid content. As a rule the analysis of a soap will aim at the determination of at least water, combined fatty acid, free fatty acid, combined alkali and free alkali.

Sampling. Considerable care must be taken to obtain a fair average sample. For desiccated, flake and powder soaps ordinary methods may be used, but for cake or bar soaps, or soaps packed in bulk in barrels, average sampling is difficult, as the outsides of the cakes or bars, or the ends and sides of the barrels are drier than the bulk of the soap. Every effort should be made to maintain the correct proportions between the drier and wetter parts of the sample. The portions of the sample should be thoroughly mixed and placed in a dry wide-mouthed stoppered bottle as quickly as possible. As soap loses water rapidly on exposure to air, it is advisable to weigh all the portions necessary for the analysis at one time, and as rapidly as possible.

Some authorities recommend weighing one or two portions only, and so arranging the determinations that the whole analysis may be completed without further weighing, but in the semi-official scheme of analysis drawn up by the American Chemical Society (p. 855) when a determination is sanctioned on a portion already used for some other determination, the remark is usually appended, that if the greatest accuracy is required a fresh portion should be taken.

The difficulty can be overcome by dissolving 20 g. of the sample in distilled water, making up the total bulk to 2000 g. with distilled water, and weighing out portions from this solution for the various determinations.

With soft soaps and certain soda soaps it is possible to substitute measurement for weighing with a consequent saving of time, but the majority of commercial soaps are thick jellies in 2 per cent. solution, and it is quite impossible to measure such solutions accurately at room temperature.

Water

This determination may for approximate purposes be carried out as follows : 10 g. of the carefully mixed sample in fine shreds or shavings is weighed into a clean, dry, tared evaporating basin, weighing a short glass rod at the same time. The evaporating basin is then placed on a sand-bath and heated at 105° to 110° with frequent stirring until a slight smell of acrolein gives warning that charring is beginning. The basin and its contents are then cooled in a desiccator, and reweighed. The difference between the first and second weighings is taken as water.

For many technical soaps such a method will be sufficiently accurate, but most natural fats contain at least a small quantity of volatile fatty acids which would be driven off and reckoned as water by such a method. If the soap under examination is derived from nut or kernel oils, *e.g.* coco-nut or palm-kernel oils, as much as 5 to 8 per cent. of the total fatty acids may be volatile.

In such soaps, and where an accurate determination of the water content of the sample is desired, it is advisable to adopt the following method :—

Water-saturated toluene is prepared by shaking toluene with water in a separatory funnel, and after settling, the excess water is drawn off, 25 to 50 g. of the sample is weighed into a perfectly dry flask, and 150 ml. of the water-saturated toluene together with a few pieces of dry pumice are added. The flask is then connected to a perfectly dry condenser, and placed in an oil-bath. Heat is applied until about 90 ml. has distilled over, the distillate being collected in a vessel which is constricted to a narrow tube at the bottom, the narrow portion being graduated in one-tenths of a ml. All the water in the sample comes over with the distillate. The condenser is washed out with a few ml.'s of toluene, and any water-drops which may have condensed on the ungraduated sides of the receiver are either tapped down or washed down with a little toluene. The distillate is allowed to settle thoroughly, and the amount of water in the sample is read off directly from the graduations on the receiver.

Two forms of apparatus are sold for this form of determination. The Hoffmann-Marcusson type consists simply of a convenient type of graduated receiver, and is designed to work with an ordinary Liebig's condenser. The Dean-Stark (Fig. 140) apparatus designed to work with an upright condenser is more highly specialized and is usually sold as a complete unit (*cf.* pp. 441-443).

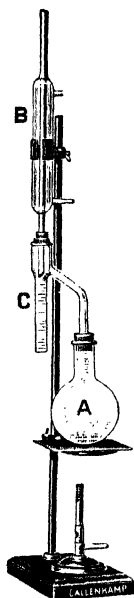



FIG. 140.
Dean-Stark Apparatus.

Total Alkali

10 g. of the sample is dissolved in 200 ml. of water and titrated with *N*/1 sulphuric acid, using methyl orange as indicator. The number of ml. of acid required $\times 0{\cdot}031 = Na_2O$ in a hard soap; in soft soaps it is usual to state the total alkali as K_2O, the factor being 0·042.

The liquid remaining from the titration may be used for the determination of total fatty acids (p. 845).

Free Caustic Alkali

Difficulties arise in this determination owing to the possibility of reaction in aqueous solution between the free alkali and free fats which may coexist with it in the soap. Formation of carbonate by exposure to the air must also be avoided.

5 to 10 g. of the sample is dissolved as quickly as possible by heating on a water-bath with 200 ml. of neutral absolute alcohol or rectified methylated spirits. The solution is filtered through a dry filter paper into another flask, keeping the funnel covered with a glass plate to avoid exposure to the air as far as possible. The filter is washed with two quantities of neutral spirit (20 ml.), and the washings added to the filtrate. Add 1 ml. phenolphthalein, and if it gives a red colour titrate with *N*/10 sulphuric acid until the colour disappears. Calculate the result to NaOH. The solution is often dark brown in colour and is apt to mask the end-point. It is then advantageous to add 1 ml. of a 0·1 per cent. solution of methylene blue in addition to the phenolphthalein. This gives a more easily observed end-point, the change being from brownish or bluish purple to a clear pale or dark green (Hilditch).

F. H. Newington [1] recommends the following alternative method for this determination. 10 g. of the sample is weighed into a 250 ml. wide-necked flask, 50 ml. freshly boiled, hot distilled water is added, the flask is lightly corked, and the whole heated on a hot plate until the soap is dissolved. 50 ml. of a hot saturated solution of neutral

[1] *J. Soc. Chem. Ind.*, 1916, 95.

sodium sulphate is now added, and the liquids thoroughly shaken together. The contents of the flask are then transferred to a separating funnel, and the flask rinsed out with a further 5 ml. of sodium sulphate solution. The separating funnel is then lightly corked and stood perpendicularly in a beaker or other convenient stand in a hot-water oven. In a very short time the soap separates out on the surface, while the liquid beneath contains any free alkali originally present in the soap. The lower solution is run off into a beaker, the separated soap washed with 50 ml. sodium sulphate solution, and the washings added to the beaker. The liquid in the beaker is then titrated with *N*/10 sulphuric acid, using a neutral 5 per cent. solution of silver nitrate as a spot indicator on a porcelain plate. So long as free hydroxide is present brown silver oxide is produced, carbonates, silicates, etc., giving no such coloration.

It is claimed that 0·01 per cent. free NaOH can be accurately determined by this method. It is only necessary to ensure the neutrality of the sodium sulphate and silver nitrate used. This method is quicker than the first method, and avoids the rather troublesome filtering of alcoholic soap solution. One of its chief advantages is that it can be applied to highly hydrated soaps without previous drying.

Alkaline Carbonate

If the alcoholic solution method is adopted for the determination of free hydroxide the alkali carbonate left on the filter paper may be dissolved in boiling water and titrated with *N*/10 sulphuric acid and methyl orange, calculating the result to Na_2CO_3.

If Newington's method is adopted it is only necessary to add methyl orange to the solution after titration of the hydroxide and continue the titration. If the soap contains silicates, borates, phosphates or other alkaline salts in addition to carbonates, it is necessary to adopt more elaborate methods of analysis. A scheme for such a detailed analysis will be found in the Standard Methods of the American Chemical Society, for which the original papers must be consulted.

The committee of the Society of Public Analysts on Soap Analysis makes the following recommendations [1] :—

Total Free Alkali

Boil 100 ml. of redistilled industrial methylated spirit (66 O.P.) in a 400 ml. flask, add 0·5 ml. of a 0·5 per cent. solution of phenolphthalein, allow to cool to 70°, and neutralize at that temperature with *N*/10 alcoholic potassium hydroxide solution. Add 10 g. of the soap in thin shavings, and dissolve as quickly as possible by heating. Immediately after complete solution of the soap add 3 ml. of *N*/1 sulphuric

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[1] *Analyst*, 1937, **62**, 36.

acid and boil on a water-bath for at least ten minutes, to ensure complete removal of carbon dioxide. If the solution is colourless, cool to 70°, and titrate back with *N*/1 sodium hydroxide until the pink colour reappears. If, after the boiling with acid, the pink colour returns, a further quantity of *N*/1 sulphuric acid must be added and the boiling repeated, the titration being completed as described above. The excess of *N*/1 sulphuric acid titrated should not be less than 1 ml. From the amount of standard acid absorbed calculate the total free alkali in terms of Na_2O (or K_2O for soft soap).

Free Caustic (Hydroxide) Alkali

(a) *Direct Titration without the Addition of Barium Chloride.* Whereas the solubility of sodium carbonate is slight and may be neglected if the soap is dissolved in alcohol of 90 per cent. strength or over, potassium carbonate is sufficiently soluble in all strengths of alcohol to introduce serious errors. The following procedure is therefore applicable to soda soaps only.

Boil 100 ml. redistilled industrial methylated spirit (66 O.P.) to remove carbon dioxide. Add 0·5 ml. of an 0·5 per cent. solution of phenolphthalein and neutralize at 70° with *N*/10 acid, or alkali. Add 10 g. of the soap in shavings or powder and heat until dissolved. Cool to 70°, and titrate at that temperature with *N*/10 sulphuric acid.

(b) *Direct Titration after the Addition of Barium Chloride.* When more than about 0·4 per cent. of total free alkali is present it is necessary to remove the carbonates with barium chloride. Dissolve 10 g. of the soap in 100 ml. of neutral industrial alcohol containing 0·5 ml. of a 0·5 per cent. solution of phenolphthalein. Add 5 ml. of hot neutral 10 per cent. aqueous solution of barium chloride in a thin stream, mix thoroughly, and titrate with *N*/10 hydrochloric acid at 70° until the pink colour disappears.

Free " Carbonate " Alkali

For Soda Soaps only. Boil 100 ml. of redistilled industrial methylated spirit (66 O.P.) in a 400 ml. conical flask, add 10 g. soap in thin shavings, and dissolve as quickly as possible by heating. Filter rapidly while hot, wash the residue on the filter with alcohol until it is free from soap and extract with hot distilled water until the washings are no longer alkaline. Titrate the combined aqueous washings with *N*/10 hydrochloric acid, using methyl orange as indicator. Calculate the result as Na_2O per cent. The determination of the alkalinity due to carbonate may be made by estimation of the carbon dioxide, for which any of the recognized methods may be used.

This is the only direct method of carbonate alkali determination applicable to potash soaps. The committee found that in the absence of interfering substances, *e.g.* silicates, phosphates, etc., the results from the carbon dioxide determination agree with those obtained by the titration of the alcohol insoluble matter, in soda soaps.

Summary of Recommendations

Sodium Soaps. The best procedure is to determine (1) the total free alkali by adding excess of mineral acid and titrating back with standard alkali; (2) caustic alkali by one of the methods described above; (3) carbonate alkali may be found by difference between (1) and (2) and may be checked by determination of alcohol insoluble alkali, or of carbon dioxide. The results of all tests of alkali in hard soaps should be expressed as a percentage of Na_2O.

Potash Soaps. Direct determination of the carbonate alkali by a titration method is not practicable. The total free alkali (1) should be determined as in soda

soaps. Free caustic alkali (2) should be determined by the barium chloride method (which is recognized as giving slightly low results). The carbonate alkali (3) is given by difference, or may be determined by the carbon dioxide method. The results of all tests of alkali in soft soaps should be expressed as a percentage of K_2O. These methods cannot be applied without modification to soaps containing phosphates, silicates, etc.

Total Fatty Acids

After the determination of total alkali has been completed, add a slight excess of sulphuric acid and heat until the fatty acids separate as a clear layer. Having reached this stage several methods of procedure may be adopted.

(*a*) If the soap is composed of fats which will give solid fatty acids, the contents of the beaker are cooled. The solid layer of fatty acids is carefully detached from the sides and the aqueous acid layer poured off. The fats are replaced in the beaker and heated with distilled water until they melt again, when they are once more allowed to cool and the wash water is poured off. Three washings should be sufficient to remove the excess of sulphuric acid. The solid cake of fatty acids is then carefully detached from the sides of the beaker, dried between folds of filter paper and weighed.

(*b*) Many soaps give soft pasty masses of fatty acids which cannot be handled in the manner described above. 10 g. of hard paraffin wax may then be added and heated along with the fatty acids. A solid cake of fat can thus be obtained, which, after washing and drying as described under (*a*), is weighed and the weight of the paraffin wax deducted. This procedure requires great care and skilful manipulation if reliable results are to be obtained. It is often exceedingly difficult to detach all the fat from the sides of the beaker, and this leads to low results. On the other hand, it is equally difficult to get rid of the last traces of water, and this has a tendency to give high results.

The following modification in the procedure is favoured by some analysts. The separation of the fatty acids is carried out in a tared beaker ; the cake of fatty acids is replaced in the beaker after the wash water has been poured off. Beaker and fatty acids are placed in a water-oven for an hour, a few drops of absolute alcohol added, and when it has all evaporated the beaker and contents are cooled and weighed. This method avoids the loss of fat on the sides of the beaker, and much better drying of the acids is obtained.

(*c*) An alternative and, in some ways preferable, method is as follows : After titrating for total alkali add a slight excess of acid and heat until the fatty acids form an oily layer. Transfer to a separating funnel, washing out the flask or beaker with 50 ml. petroleum ether. When sufficiently cool add a little more petroleum ether, place

the stopper in the separating funnel, shake up the contents, and allow to settle. Run off the aqueous acid layer into a beaker. Wash the petroleum ether extract twice with 50 ml. warm (not hot) water, adding the washings to the acid liquor. Place the acid liquor in another separating funnel and add a further 50 ml. petroleum ether. Shake up, settle, separate, and wash as before. Collect the two petroleum ether extracts in a weighed beaker, evaporate the spirit and weigh the residual fatty acids. If there should be difficulty in obtaining a good separation of the water and petroleum ether layers, the addition of 5 or 10 ml. of a saturated solution of sodium chloride will usually bring about the separation. The weight found by any of these methods is the amount of fatty acids obtained from the sample. If, in the final statement of results, it is intended to report the alkali as oxide of sodium or potassium, it will be necessary to calculate the fatty acids to anhydride. To do this exactly presumes a knowledge of the mean molecular weight of the fatty acids, and if deemed necessary this can be calculated from the saponification equivalent, but it is customary in the analysis of textile soaps to multiply the weight of fatty acids by 0·97 and to accept the product as a satisfactory approximation.

A method of estimating the fatty acids by means of their refractive index has been published by Leithe and Heinz.[1]

2 g. of washing powder or finely divided soap and 10 ml. 10 per cent. sulphuric acid are heated to boiling in a 30 to 50 ml. Jena glass tube provided with a glass stopper. 3 ml. of α-bromonaphthalene is added and the warm mixture shaken vigorously for one minute. A drop of the clear bromonaphthalene solution is transferred to the prism of an Abbé refractometer and the refractive index (n^{40} solution) determined at 40°. The refractive index of the fatty acids themselves (n^{40} fatty acids) is then determined.

3 g. of soap or 5 g. of washing powder and 10 ml. 20 per cent. sulphuric acid are heated in a centrifuge glass tube, and shaken until the fatty acids begin to separate as an oily layer, and then centrifuged. A drop of the clear fatty acids is placed in the refractometer and its refractive index determined at 40°. The percentage of fatty acids in the sample may then be calculated as follows :—

$$\text{Per cent. fatty acids} = \frac{V \times d}{w} \times \frac{n^{40°}\text{ bromonaphthalene} - n^{40°}\text{ solution}}{n^{40°}\text{ solution} - n^{40°}\text{ fatty acids}} \times 100.$$

V is the volume of bromonaphthalene at 40° ; d is the density of the fatty acids at 40°, which averages $0{\cdot}885 \pm 0{\cdot}002$ in washing powders, and $0{\cdot}890 \pm 0{\cdot}005$ in soaps ; w is the weight of soap or washing powder.

[1] *Angew. Chem.*, 1936, **49**, 412-414.

It is claimed that the method is rapid and accurate, but on account of the special type of apparatus necessary it is not likely to become generally used.

Free Fatty Acids

The usual method of making this determination is to place 10 g. of the sample, which has been dried at 100° to 105° (see Determination of Water, p. 841) in a 250 ml. Erlenmeyer flask, and add (*a*) 50 ml. neutral alcohol, *or* (*b*) 25 ml. neutral methyl alcohol and 25 ml. toluene, *or* (*c*) 25 ml. neutral alcohol and 50 ml. petroleum spirit (B.P. about 80°). The contents of the flask are freely boiled for not more than two minutes, a few drops of phenolphthalein added, and titrated against *N*/10 alcoholic potash until a semi-permanent pink colour appears. Solvent (*b*) and (*c*) are more satisfactory than (*a*).

To avoid the difficulty in bringing the soap into solution in a flask, some operators prefer to extract the soap with neutral petroleum ether in a Soxhlet apparatus. The sample is weighed in a glass vessel similar to a weighing bottle, but with perforations in the bottom and lid. The holes at the bottom are covered with ignited asbestos fibre, over which a layer of filter paper, and finally a glass disc with fine perforations, are placed. The bottle thus prepared is dried at 105° for an hour, cooled in a desiccator, and weighed. The loss in weight gives the amount of water in the sample.

The bottle, without the lid, is then placed in the extractor, and its contents extracted with neutral petroleum ether for about six hours. If the material left in the bottle is dried and weighed it will give the amount of " filling " in the soap.

The solution is titrated with *N*/10 alcoholic potash, using phenolphthalein as indicator, as before. The free fatty acids are usually stated in terms of the acid present in greatest amount. Thus ml. *N*/10 alcoholic potash consumed, multiplied by 0·0282 equals oleic acid; multiplied by 0·0256 equals palmitic acid; and multiplied by 0·0298 equals ricinoleic acid. In soaps containing a considerable quantity of nut oils an average factor of 0·022 is often employed to allow for the presence of lauric acid with a molecular weight of 200.

A committee of the Society of Public Analysts has made the following comments and recommendations regarding the determination of free fat.[1] They recommend the following definitions :—

(a) *Unsaponified neutral fat* for the unsaponified glycerides.

(b) *Total unsaponified matter* for the sum of the free fatty acids, unsaponified neutral fat, and unsaponifiable matter.

(c) *Total free fat, or total unsaponified saponifiable matter*, for the sum of the free fatty acids and the unsaponified neutral fat.

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[1] *Analyst*, 1935, 60, 537.

The committee recommends that the following three determinations should be carried out :—

(1) *Free fatty acids* by direct titration.

(2) *Unsaponified neutral fat* together with unsaponifiable matter, by the prescribed method of extraction.

(3) *Unsaponifiable matter* by saponification and extraction of (2).

Hence unsaponified neutral fat is (2)—(3), and total free fat, or unsaponified saponifiable matter (2)—(3)+(1).

Free Fatty Acids

Boil 100 ml. of redistilled industrial methylated spirit (66 O.P. or 94·7 per cent. by vol.) in a 400 ml. conical flask, add 0·5 ml. of an 0·5 per cent. solution of phenolphthalein, allow to cool to 70°, and neutralize at that temperature with *N*/10 alcoholic potash until a faint pink colour persists for fifteen seconds, maintaining the temperature at 70° throughout the titration.

Calculate the percentage of free fatty acids in the soap from this titration, expressing it as a percentage of oleic acid (mol. wt. 282).

The results may be expressed in terms of some other acid of different molecular weight, provided that it is clear that this has been done. It may be desirable to determine the mean molecular weight of the fatty acids present after separating them from the soap, when the molecular weight found and used should be distinctly stated. In soaps containing an unusually large proportion of matter insoluble in alcohol it may be desirable to filter the solution before titration, but such a procedure may cause a slight increase in the apparent free fatty acids present.

Unsaponified Neutral Fat and Unsaponifiable Matter

Weigh 5 g. of the soap in thin shavings and dissolve in about 80 ml. of a mixture of 50 ml. redistilled industrial methylated spirits (60 O.P.) and 100 ml. water, without heating more than is necessary. Transfer the solution to a 500 ml. separating funnel, washing the beaker with the remaining 70 ml. of the dilute alcohol. Extract with 100 ml. of ethyl ether while still slightly warm, run off the alcoholic soap layer into a second separating funnel and repeat the extraction with a further 50 ml. of ether. Extract the lower layer again with a further 50 ml. of ether, and pour the three ethereal extracts into a separating funnel containing 20 ml. of water. Rotate the separating funnel gently without violent shaking, and after allowing to separate, run off the wash water. Repeat the washing with water in this way until the water run off is not more than faintly turbid on acidification. Wash the ethereal solution twice further by shaking vigorously with 20 ml. of *N*/2 aqueous potassium hydroxide, each washing with alkali being immediately followed by washing with 20 ml. of water,

shaking vigorously each time. Acidify the last washing with alkali after separating it, and if the liquid becomes turbid, repeat the washing with alkali and water until the final washing with alkali remains clear on acidification. Finally wash with successive quantities of 20 ml. of water until the washings no longer give a pink colour with phenolphthalein. Transfer the ethereal solution to a weighed flask and distil off the ether. When nearly all the ether is evaporated add 2 or 3 ml. of acetone. By a gentle current of air remove the solvent completely from the flask, which is preferably almost entirely immersed, held obliquely, and rotated in a boiling water-bath. Repeat this operation until the weight is constant.

The residue obtained consists of unsaponified neutral fat and unsaponifiable matter. After weighing, dissolve the contents of the flask in 10 ml. of freshly boiled and neutralized industrial spirit and titrate with $N/10$ alcoholic potassium hydroxide to phenolphthalein. Not more than 0·1 ml. should be required for neutralization. If more is needed the test has not been effectively carried out, and must be repeated.

Unsaponifiable Matter

Evaporate the solution remaining from the above titration until the bulk of the alcohol is removed. Add 25 ml. of $N/2$ alcoholic potassium hydroxide and boil under a reflux condenser for thirty minutes. Transfer the alcoholic soap solution to a separating funnel by the aid of 50 ml. of water, and repeat the process of ether extraction, washing, etc., described above. Weigh the final residue of unsaponifiable matter. Subtraction of this weight from the weight obtained above gives unsaponified neutral fat.

The following are comments by the committee of the Society of Public Analysts :—

Much attention has been given to the precise conditions for the titration of free acidity. It has been found necessary to adhere closely to the conditions laid down in the above description for accurate results. The following points resulting from the work on the subject are worthy of mention.

The Indicator. It has been found by electrometric methods that, in the titration of fatty acids with alcoholic potassium hydroxide at 70°, the point of neutralization corresponds sufficiently closely for practical purposes to the change of colour of phenolphthalein when 0·5 ml. of a 0·5 per cent. alcoholic solution of the indicator is present in 100 ml. of the alcoholic soap solution. More gives low results, and less gives high results. This indicator is therefore the most suitable for the titration.

Filtration. A faintly alkaline alcoholic solution, with or without soap, becomes less alkaline or even slightly acid to phenolphthalein after filtration. The chief cause of this production of acidity is the absorption of carbon dioxide during filtration, although there are other factors involved. In the determination of free fatty acids in a soap which is only faintly acid, filtration may give rise to an error of the order of 0·3 ml. $N/10$ on 5 g. of soap, or a soap which is faintly alkaline may be made to appear slightly acid by filtration, but these errors are negligible when appreciable quantities of free fatty acids are present.

Alternative Methods. Two variations in the titration method may be found useful in certain circumstances.

Barium Chloride Method. There is a possibility of the co-existence in soap of free fatty acid and sodium carbonate. When such a soap is dissolved in alcohol some interaction takes place, although if dry sodium carbonate is added to an alcoholic solution of soap containing free fatty acids, no reaction takes place. Free fatty acid may be titrated in the presence of sodium carbonate by adding 1 ml. of a neutral 10 per cent. aqueous solution of barium chloride to the neutralized alcohol, dissolving the soap in the boiling mixture, and titrating the free fatty acids without filtration. The effect of the sodium carbonate is thus eliminated.

Glycerine Method. In order that the titration may be carried out at laboratory temperature without jellying of the soap solution, a mixture of alcohol and glycerine may be used (80 : 20 by vol.) as the solvent. In preparing this, a slight excess of alkali should be added to the glycerine-alcohol mixture, and the whole saponified, then made slightly acid, and adjusted to neutrality to phenolphthalein at 15° by the cautious addition of *N*/10 alcoholic potassium hydroxide. 5 g. of soap is soluble when warmed with 100 ml. of this solvent, and accurate results are obtained at 15°.

Rosin Acids

Rosin consists almost entirely of complex terpene acids with a mean molecular weight round about 325, with small proportions of gumlike or resinous materials and certain mechanically retained vegetable impurities. The principal acids present are abietic acid ($C_{20}H_{30}O_2$), and pimaric acid ($C_{20}H_{30}O_2$). The rosin acids and anhydrides combine readily with alkalis (either in the form of caustic or carbonate) on boiling; and the presence of their alkali salts in a soap often improves the lathering properties and consequently the detergent powers of the soap. Any rosin acids present in a soap are weighed along with the fatty acids in the determination of total fatty acids. When a soap is bought and sold on the understanding that it contains rosin it is often sufficient to determine total rosin and fatty acids together.

The proportion of rosin to fat in genuine rosined soaps is usually in the neighbourhood of 1 : 10; and very rarely exceeds 1 : 3. On the other hand, the presence of rosin in a soap is objectionable when the soap has to be used in certain textile processes, and if the presence of rosin is suspected it should be tested for, and if found it should be estimated.

Qualitative Test (*Liebermann-Storch*).—1 to 2 ml. of the separated fatty acids are gently warmed in a test-tube with 10 ml. acetic anhydride and cooled. The acetic anhydride layer is withdrawn to another test tube and shaken with a drop of sulphuric acid 62 per cent. (105° Tw.). If a green-violet or green coloration is produced there is a probability that rosin acids are present, and the determination should be proceeded with. However, many other terpene derivatives give colorations with this test.

Quantitative Determination (*Twitchell Method*).—Weigh accurately into a 300 ml. beaker 5 g. of the sample and dissolve in 200 ml. hot water. Add 20 ml. dilute sulphuric acid (1 : 4) and heat until the fatty acids separate as a clear layer. Cool and transfer to a separatory funnel. Wash the beaker with two 20 ml. portions of ethyl ether and add to the liquid in the funnel. Add a further 20 ml. of ether and shake well. Allow the ethereal solution of the fatty acids to separate, draw off the watery solution, and wash the ethereal solution with water until the washings are free of acid. Should there be a difficulty in obtaining good separation during washing, a little salt may be added to the wash water.

Transfer the ethereal solution to a 200 ml. Erlenmeyer flask, evaporate off the ether, add 5 to 10 drops of absolute alcohol and heat at 105° for a further twenty minutes. Now dissolve the mixed fatty and rosin acids remaining in the flask in 30 ml. of absolute alcohol. A stream of hydrochloric acid gas, dried thoroughly by fused calcium chloride, is passed through the alcoholic solution for one hour, the flask being kept cool by standing it in a vessel through which cold water is circulating. Allow the reaction to proceed by setting the flask aside for a further hour, then add 150 ml. of water and boil for five minutes. The mixture is then transferred to a separatory funnel, the flask being washed out with 150 ml. ether, and the ethereal solution of the products of the reaction is washed with water until neutral. The bulk of the ether is then evaporated, 50 ml. of neutralized alcohol added, and the solution titrated to phenolphthalein with standard caustic alkali. The mean equivalent of rosin acids is usually assumed to be 346, so that

$$\text{Percentage of rosin acids} = \frac{\text{ml. N. alkali} \times 0{\cdot}346}{\text{weight of sample}} \times 100.$$

Fortini Method.[1]—Fortini takes exception to the Twitchell method because rosin-free soaps are apt to show a rosin content by that method. He recommends the following procedure :—

2 g. of the fatty acids from the suspected sample are treated in a separatory funnel with 50 ml. petroleum spirit. 10 ml. of nitric acid, prepared by mixing 1 part fuming acid (sp. gr. 1·52) and 3 parts acid (sp. gr. 1·48) and treated with a little urea to destroy any nitrous acid, is gradually added, shaking vigorously after each addition. After standing, the acid layer is drawn off and the ether layer again shaken with 5 ml. of the prepared acid, which, after settling, is run off. The ethereal layer is then washed with ordinary nitric acid and finally with water until acid-free. It is then filtered through a dry filter paper which is washed several times with ether, and the ethereal solution evaporated to dryness and weighed. This weight represents the fatty

[1] *J. Soc. Chem. Ind.*, 1918, 381 A.

acids only, as the nitrated resin acids are insoluble in ether. The method is quicker and involves fewer transferences from one vessel to another, and as the Twitchell method is admittedly approximate, it will probably be equally reliable if skilfully carried out.

Volatile Fatty Acids

Soaps containing fats derived from nuts and nut kernels contain considerable quantities of volatile fatty acids. The determination of total fatty acids in such soaps requires special care, otherwise a portion of these volatile acids may be lost. In particular, the heating of the fatty acids with dilute acid, and with the wash waters, should be as short as possible, should be kept to as low a temperature as will serve to separate the fat, and boiling never permitted. It is often of interest to determine the amount of volatile acids present, and this can be done as follows :—

Polenské Method.—The total fatty acids are first of all determined in the usual way. A quantity of soap equivalent to 10 g. of the fatty acids is weighed into a flask—thus in the case of a 60 per cent. soda soap 16·6 g. is taken, and with a 40 per cent. potash soap 25 g. and water added to make up the weight to 200 g. The flask is heated on a water-bath until the soap is completely dissolved, and the solution is acidified with dilute sulphuric acid (1 : 4), using methyl orange as indicator. Heating is continued until the fatty acids melt completely, and the aqueous liquid is quite clear. The liquid is transferred to a separating funnel, the aqueous layer run off, the fatty acids shaken with four successive quantities of hot water, and the clear acids filtered through a thick dry filter paper. 5 g. of the prepared fatty acids are weighed into a dry 300 ml. flask, 2 ml. of 50 per cent. caustic soda added, and the flask heated with constant agitation until the liquid clarifies. Cool to 100°, add 100 ml. of boiling water, and allow the soap to dissolve. Add 0·1 g. powdered pumice and decompose with 40 ml. of 6 per cent. sulphuric acid. Connect the flask with a condenser, heat gently until the fatty acids are melted and distil over 110 ml. in from nineteen to twenty-one minutes.

The distillate is placed in water at 15° for fifteen minutes and then filtered through a wet filter paper. The condenser and receiver are washed through with 18 ml. of cold water which are used to wash the fatty acids on the filter. The condenser is then cleansed with four successive washings of 10 ml. of neutral alcohol, which are run into the receiver, poured over the filter, and collected in a titrating flask, and the mixed alcoholic solutions titrated with $N/10$ alcoholic potash, using phenolphthalein as indicator. These volatile fatty acids consist almost entirely of a mixture of caprylic acid ($C_8H_{16}O_2$,

mol. wt. 144) and capric acid ($C_{10}H_{20}O_2$, mol. wt. 172) in varying proportions ; *e.g.* in coconut kernel oil the proportion is roughly 2 : 1, while in palm kernel oil it is almost 1 : 1 ; but for practical purposes it is sufficient to assume a mean molecular weight of 158, therefore 1 ml. $N/10$ alkali = 0·0158 g. volatile fatty acids.

Mean Molecular Weight of Fatty Acids

This value may be determined by dissolving a weighed portion of the separated fatty acids in neutral alcohol and titrating with $N/1$ alcoholic potash. Then :

$$\text{Mean Mol. Wt.} = \frac{\text{Weight of Fatty Acids} \times 1000}{\text{ml. } N \text{ alkali consumed.}}$$

Conclusions

When the various determinations have been completed, adjustments have to be made before a final report can be drawn up.

If free fatty acids, unsaponified neutral fat, and volatile fatty acids are to be reported separately, the amount of these items should be deducted from the total fatty acids, and the remainder reported as combined fatty acids, or anhydrides. If they are to be reported as anhydrides the weight of fatty acids must be multiplied by 0·97.

The total alkali is usually calculated as Na_2O, and the Na_2O equivalent of the free caustic alkali and the alkaline carbonate deducted from the total, and the remainder reported as combined Na_2O.

The various items may be reported as follows :—

Combined fatty anhydrides.
Free fatty acids.
Uncombined neutral fat.
Combined alkali, Na_2O (or K_2O).
Free caustic alkali, NaOH (or KOH).
Alkali carbonate Na_2CO_3 (or K_2CO_3).
Rosin acids (if any).

The interpretation of a soap analysis depends to a very large extent on the purpose for which the soap is intended, and may require to be supplemented by details other than those supplied by a quantitative analysis. Such an analysis will inform one what is the amount of actual soap in the sample, and whether or not it has been well made. When buying a known type of soap and merely requiring it to be kept up to standard the analysis may suffice, but it is only of very limited value when comparing unknown qualities with one another. Soaps which are intended for the scouring of coloured goods should, as a general rule, contain not more than a trace of free caustic alkali.

Textile soaps should be free from fats which develop an offensive

odour on ageing, for although pure cellulose adsorbs very small quantities of soap, coloured goods frequently adsorb quite considerable amounts, and soaps which produce ill-smelling products on ageing give rise to much trouble when goods treated with them are stored. In woollen goods, which adsorb much more soap, this is even more important. Such soaps also frequently cause yellowing of the whites on storage. The desirability or otherwise of the presence of alkaline carbonates, silicates, phosphates, and colloidal clay must also be decided by the specific purpose for which the soap is required.

Unfortunately the comparative values of soaps often depend on qualities which are not easily measured. The most important of these is the "detergent" or "cleansing" power. It is probable that what is termed "detergent power" is dependent on several distinct qualities which are difficult to measure individually and co-ordinate so as to give a reasonable measure of "detergency." Of the methods which seek to estimate "detergency" on the basis of the measurement of one essential property, probably that based on the "Donnan drop number" has received most attention. Trotman, Cobb, Simm and others have shown that this method is subject to such variations that it is quite impossible to compare one set of results with another. In particular, it was found that soap solutions aged for from 10 to 150 minutes increased their drop numbers by from 32 to 400 per cent.

The method worked out by McBain and his co-workers in which the amount of suspended carbon carried through a filter by soap solutions is measured tintometrically has not met with general acceptance. It has been criticized mainly because the conditions are difficulty to standardize and the procedure is tedious; many critics maintain that the test measures only the peptizing power of the soap which is only one factor in detergency. "Lather number," "lather volume," "lather persistence," and "specific viscosity" of soap solutions have also been used to measure detergent power (see also p. 830).

Such methods have not yet become sufficiently standardized for general use in the commercial testing of soaps, but they serve to indicate the lines along which the usual analysis will probably be supplemented in the future. All the authorities agree that in the range of compounds generically termed fatty acids only those containing from six to twenty-two carbon atoms form alkali salts of a soapy nature. The acids containing more than twenty-two carbon atoms give alkali salts of such slight solubility that their soapy character is quite lost. The soapy qualities reach a maximum at C_{16}, so that in a general way one may say that the best soaps are made from fatty acids having from fourteen to eighteen carbon atoms in the molecule, *i.e.* mean molecular weight 228 to 284. Thus the determination of the mean

molecular weight of the fatty acids may be used as an indication of the suitability of the fats employed.

Some form of practical test to estimate the value of a soap for the particular purpose for which it is required is useful. Where the principal quality to be determined is "detergency," the majority of such tests depend upon the removal of "dirt" from an artificially soiled fabric. Of such methods the following is probably as serviceable as any :—

A well-scoured botany serge is artificially dirtied by padding through a solution of lanoline in benzene in which a quantity of lamp black has been suspended. A series of solutions of the soaps to be compared are made up at, say, 0·2, 0·25, 0·5 and 0·75 per cent. Weighed portions of the synthetically dirtied material are scoured in these solutions for half an hour at 60°, using a 30 : 1 liquor-material ratio, care being taken to give each sample as nearly as possible the same mechanical treatment. In this way two series of patterns ranging from deep grey to white are obtained. By visual examination of the patterns the concentration of the different samples which give approximately the same degree of cleanliness is observed and the detergent power of the samples expressed in terms of concentration. Thus, if 0·25 per cent. of sample A gives the same degree of cleanliness as 0·5 per cent. of sample B, then A is said to be twice as efficient as B. The usefulness of the method may be extended by determining the amount of lanoline in the original soiled pattern, and then determining the percentage of that amount removed by each concentration of soap and plotting lanoline removed against concentration of solution.

Bosshard and Sturm [1] have proposed a modification of this method. The soiled fabric is prepared by precipitating a known amount of ferric oxide in it, and impregnating it with a known quantity of oil or fat. The prepared fabric is scoured under controlled conditions as above. The strip is dried, a portion of it is ashed and the residual iron oxide in the ash determined. The proportion of fat or oil left after scouring is determined in another portion.

THE AMERICAN CHEMICAL SOCIETY'S SCHEME OF ANALYSIS

A comprehensive scheme for the sampling and analysis of soaps has been published by the American Chemical Society.[2] It has been criticized on the grounds that it requires much larger samples than are often available, and that the scheme of analysis is unnecessarily complex for ordinary commercial requirements. Many of the methods recommended only vary in detail from those given above, but methods are included for the determination of glycerol, sugar, starch and volatile hydrocarbons.

[1] *Chem. Zeit.*, 1930, 54, 762.

[2] *Ind. Eng. Chem.*, 1922, 14, 1159.

Glycerol, Sugar and Starch

1. **Glycerol in the Absence of Sugar.**—*Solutions Required.* Potassium dichromate, 74·552 g. per litre; sodium thiosulphate, *N*/10; potassium iodide, 10 per cent.

Dissolve an accurately weighed sample of the soap,[1] equivalent to not more than 3 g. of glycerol, in 200 ml. water in a 600 ml. beaker. Decompose with 25 ml. sulphuric acid (1 : 4). Cool, remove and rinse the cake of fatty acids, transfer the acid water and rinsings to a 500 ml. graduated flask, add about 0·25 g. silver sulphate to precipitate traces of chlorides and soluble fatty acids. Make up to the volume and mix contents thoroughly. Transfer a filtered, accurately measured, 50 ml. aliquot of the above to a 400 ml. beaker. Add 75 ml. accurately measured potassium dichromate solution, followed by 25 ml. sulphuric acid (sp. gr. 1·84). Cover with a watch-glass and oxidize by heating in a steam-bath for three hours. Conduct a "blank" in like manner using 100 ml. water, 25 ml. sulphuric acid (sp. gr. 1·84) and 25 ml. accurately measured potassium dichromate solution. Cool, and make up the solutions to 1000 ml. in graduated flasks. The excess of potassium dichromate is determined by taking a 50 ml. aliquot of the above, adding 50 ml. water, 20 ml. 10 per cent. potassium iodide solution, and titrating the liberated iodine with *N*/10 thiosulphate, using starch as indicator. Calculate the percentage of glycerol. (1 ml. potassium dichromate solution equals 0·0100 g. glycerol.)

2. **Sugar.**[1]—Dissolve 10 g. of the soap in 200 ml. hot water in a 600 ml. beaker. Decompose with 25 ml. sulphuric acid (1 : 4), boil gently for twenty minutes to invert the cane-sugar completely. Cool, remove and rinse the cake of fatty acids. Extract the acid liquid with 25 ml. ether. Transfer the acid liquid to a 500 ml. graduated flask, make up to volume and mix thoroughly. Determine the invert sugar in 50 ml. of this solution by the Munson-Walker method.[2] To calculate sugar (sucrose) multiply the amount of invert sugar found by 0·95.

3. **Glycerol in the Presence of Sugar.**[3]—Proceed as above under (1), taking a sample so that the sum of glycerol and sugar is not more than 3 g.[1] The solution must be boiled in all cases for at least twenty minutes to ensure complete inversion of cane sugar. Determine the amount of potassium dichromate solution required to oxidize both the sugar and the glycerol. Determine also the sugar by the method given in (2). Calculate the percentage of glycerol after deducting

[1] If starch is present it will be necessary to remove the matter insoluble in water.

[2] *J. Amer. Chem. Soc.*, 1906, **28**, 663; *Bureau Chem. Bull.*, 107; *Methods of Analysis of Assoc. Offic. Agr. Chem.*, 1920, 78.

[3] Hoyt and Pemberton, *Ind. Eng. Chem.*, 1922, **14**, 54, 340.

the amount of potassium dichromate required by the sugar. 1 ml. potassium dichromate solution equals 0·0100 g. glycerol. 1 ml. potassium dichromate solution equals 0·01142 g. invert sugar.

4. **Starch.**[1]—Separate the matter insoluble in water, using a sample of soap that will not give more than 3 g. of starch. Transfer the insoluble matter, without drying, to a flask and heat for two and a half hours with 200 ml. water and 20 ml. hydrochloric acid (sp. gr. 1·125) under a reflux condenser. Cool and nearly neutralize with sodium hydroxide. Make up the volume to 250 ml., filter, and determine the reducing sugars by the gravimetric method as given under determination of sugar (p. 856). Calculate the amount of dextrose (d-glucose) equivalent to the copper oxide obtained. This multiplied by 0·90 equals the amount of starch.

Volatile Hydrocarbons

Weigh not less than 250 g. of the sample into a 5-litre flask which can be heated on a gauze. Add 2 to 3 litres of distilled water. Place a two-holed rubber stopper in the flask, through one hole of which is inserted a copper or brass tube extending into the flask and terminating in a small circular ring of the tubing, bent so that the ring is in a horizontal position. Numerous small holes are drilled in the upper side of this ring and the end of the tube is sealed. This ring should be near the bottom of the flask.

Through the other hole of the stopper is inserted a glass tube provided with a trap of suitable form, the upper end of which is connected with a plain Liebig condenser. The end of the condenser tube is bent so as to extend into a burette graduated to 0·1 ml.

Introduce steam (free from oil) into the flask through the brass tube and collect the distillate in the burette. When the burette becomes full draw off the water by opening the stopcock. The foam which forms in the flask may be controlled by momentarily shutting off the steam, and by regulating the heat applied to the flask.[2] Read from time to time the amount of hydrocarbon distillate which collects on the top of the water in the burette, and when there is no further increase in this distillate the operation is finished. Allow the burette to stand overnight, tightly stoppered, and then after reading the amount of distillate, draw off the water as carefully as possible.

Determine the specific gravity of the distillate, and calculate the weight and percentage in the original sample.

[1] *Methods of Analysis, Assoc. Offic. Agr. Chem.*, 1920, 95; *Bureau of Chem. Bull.*, 107, 53.

[2] Some analysts find it an advantage to add 200 to 300 g. calcium chloride to the flask containing the soap solution to prevent foaming.

XII. EXAMINATION OF TEXTILES AFTER FINISHING

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THE examination and testing of finished textile goods involves the necessity for detecting defects which may cause dissatisfaction in use, and for defining and measuring the qualities which determine the behaviour and endurance of the fabric in the varied conditions to which it may be subjected by the consumer. Permanence of colour and finish has improved greatly during the past twenty years, and among other effects has restricted the application of methods depending upon colour reactions, swelling, and absorption in the examination of textile finishes to a small percentage of the cases met with in practice.

In the account which follows an endeavour has been made to enumerate the properties of a fabric which affect the behaviour in use, the principal methods by which the properties are modified, and the defects which may arise from such operations; finally, methods are suggested by which the effect of the modification may be assessed. Most of the properties described are complex functions of several variables, and the author has been guided by experience rather than by precept, since the application of rigorous methods is possible only when rigorous definition has been achieved.

A functional classification has been adopted to facilitate reference, since the questions which usually arise in practice are the identification of the method by which a given property has been given to a fabric, and the comparison of two samples in respect of a property. Enumeration in this manner is, however, very important for a second reason which may be exemplified by the condensation upon a fabric of methylolurea resins: this substance is used for the fixation of dyestuffs, starches, other stiffening agents, pigments, embossed effects, waterproofing agents, mordanting, stiffening, weighting; for the prevention of shrinkage, reduction of lustre, improvement of light fastness, and fixation of temporary set in yarns or filaments, in addition to the primary use in reducing elastic after-effect. Each of these uses has been patented by one or more interested parties, hence the selection of the desired effect is a matter of primary importance, and determines to whom the royalty shall be paid. The identification of the resin in a finish is of little value. In a lesser degree the same is true of almost every method of permanent and semi-permanent finishing mentioned in this section; many of the patents would not withstand opposition.

Finally, the importance of physical measurements, especially

load/extension cycles taken to progressively increasing loads, must be stressed. The application of colour reactions, tests based upon selective absorption and swelling reactions, becomes progressively more restricted, as white finishes diminish in proportion to dyed effects, while high temperature treatments, and chemical finishes are found upon an increasing proportion of textile goods. Chemical methods can be used only with much caution, since there is scarcely one standard method which is not likely to fail in an increasing number of cases, while the results of physical tests frequently restrict the possibilities to a reasonable number, among which discrimination by chemical methods becomes possible.

A. Softness

The properties grouped under the commercial term "softness" comprise low coefficient of friction superficially and internally, and low resistance to distortion in all directions. The composite property is largely determined by the construction of the fabric, but is influenced by almost all preparatory and finishing operations. "Harsh" and "papery" finishes probably occur more frequently than all other finishing defects together, and the sources of the trouble are correspondingly many.

The principal methods of finishing employed to produce softness are here enumerated, and the sources of defects indicated; many of these do not necessarily arise from the finishing methods, but from prior processes.

1. Mechanical Processes

Finishes which improve the smoothness of the fabric by mechanical means involve pressure upon the surface. The operations of calendering, chasing, pressing, the similar process of jacking, and occasionally a very short beetling operation are used, but the extent of smoothing desired is much smaller than that required for improved reflection of light, since setting of the yarns involves increased resistance to angular distortion, thus impairing the draping qualities. An operation allied to calendering which is employed purely to reduce the surface projections to an even level without much detriment to the draping qualities, consists in pressing the cloth upon a heated cylinder by means of a blanket (Palmer machine).

Faults.—Owing to the gentle nature of the above smoothing processes mechanical damage is rare, and the only trouble of common occurrence is the bruising or cutting of fabrics in a series of small creases one or two inches long running diagonally inward from the selvedges. These arise from differences in shrinkage between the selvedge and the body of the fabric, due either to differences in the

tension between the yarns during or prior to weaving, or to the use of yarns which had not the same properties, although tension in the loom state did not differ; the use of cotton selvedge yarns together with a regenerated cellulose warp is a common instance. The selvedges may be shorter or longer than the fabric itself, the cases being evident on simple inspection. The allocation of responsibility for the defect is sometimes less simple.

If a reference sample of the fabric in the loom state is available, the behaviour of the two sets of yarns in respect of extension under load, and shrinkage when dried without tension after relaxation in the conditions which caused the defect, may be observed.

The defect may, however, be caused in finishing processes, if the selvedge, though otherwise suitable, differs in thickness from the fabric. Goods processed in the open width, especially fabrics of regenerated cellulose or cellulose acetate, are wound in the wet state upon rollers in certain types of plant (jig dyeing machines, open-width centrifuges, padding machines); the selvedges do not make a cylinder of the same radius as the bulk of the pieces, and are therefore subject to greater or smaller tension according as the selvedge is thicker or thinner than the fabric. If the selvedge is not extensible to the necessary extent, breakage may occur when it is thicker. If the selvedge and warp yarns of the loom state samples behave similarly in respect of shrinkage or extension, the fault is clearly due to the finishing.

When such a standard is not available the crimp and load extension curves of the selvedge and warp threads from the defective goods must be compared. If it is found that the tight set of yarns could have been extended to correspond with the slack set, without excessive tension, the defect is due to manipulation. If, on the other hand, the two sets could not have been extended to the same length under the safe limit of tension the fabric itself must be considered defective.

After the above-mentioned operations, loss of tensile strength is frequently found in fabrics which have been treated for prevention of creasing or shrinking with formaldehyde or formaldehyde resins. The bruising and rupture of the fibres or filaments is then readily visible under the microscope. Linen is sometimes more susceptible to damage from this cause than cotton.

2. Softening Agents

Finishes which depend upon the deposition of a film of lubricant upon the surface of the fabric or throughout the yarns are used almost universally for dress fabrics. The low coefficient of friction increases the extensibility, flexibility, wear, and apparent tensile and ripping tests: for this reason goods which have been damaged are heavily

lubricated in order to disguise the defects, and should be freed from fatty matter before mechanical tests are executed. Ruptured filaments in cloths of silk and artificial silk are coated upon the surface with a film of lubricant, in order to reduce the dispersion of light at the defective places, for which reason wear tests upon unextracted fabrics should be determined upon both sides of the fabric. Also some fabrics (*e.g.* poplins) resist wear better on one side than on the other, owing to attempts by weavers to obtain better " cover " on the face.

Softening agents may be divided into two groups: hygroscopic substances such as glycerol, urea, sodium lactate, calcium chloride, magnesium chloride, di- and tri-ethanolamines; and fatty substances, which may include mineral and vegetable oils, soaps, fats, together with fatty substances containing one or more hydrophilic groups and several hydrocarbon residues.

Occasionally salts of quaternary bases are used as softening agents, usually as hydrochlorides or hydrobromides; this practice is dangerous, since when the fabric is ironed or exposed to light the mineral acid is liberated and rapidly hydrolyses the fibre. Wool is little affected but natural silk and cellulosic fibres are readily tendered.

Faults.—The faults likely to arise from the use of softening agents, apart from general or local excess or deficit, are few in number.

Reduction in Lustre. This is perhaps the most common fault, and is more widespread than is generally realized. The fatty group of softeners is usually responsible, and the degree of dulling can be estimated by comparison of extracted and unextracted samples.

Washing in a liquor containing 1 per cent. sodium oleate, 1 per cent. Emulphor EL, 1 per cent. Calgon at 60° to 100° for thirty minutes will remove most fatty softening agents.

Rancidity. Development of rancidity appears to bear some relationship to the iodine value of the fat, but in practice olive oil, for example, behaves satisfactorily if of good quality, and bad cases are usually found to contain iron, copper or manganese.

Storage in a stoppered jar at a temperature of 50° to 60° soon causes rancidity to develop: if after a few days no odour is observed the defect is unlikely to arise.

Lack of Fastness to Light. The application of fatty compounds containing a great diversity of groups (basic, acidic and neutral, saturated and unsaturated) has brought to light an increasing number of cases of anomalous fading, chiefly among the soluble dyestuffs, direct, acid and basic. The dyestuff is sometimes associated with a fat more intimately than with the fibre, especially when preparation in a fatty compound capable of forming a complex with the dyestuff precedes the dyeing process, or when the fatty matter is added to the dye-bath. The fastness to light of such dyeings is usually poorer than that of the

untreated dyeing, and the fastness to detergents and dry cleaning may also be affected. Consequently the fastness properties of a dyestuff cannot be taken for granted apart from tests in the specific finish, and constant control is necessary in order to ensure the maintenance of a standard of fastness. When salts of aliphatic cations with mineral acids are used as softening agents the tensile strength of the fabric should be examined after exposure to light.

3. Breaking Processes

Breaking processes have as their object the reduction of cementation or cohesion between fibres or filaments, and between warp and weft, in order that resistance to distortion in any manner shall be reduced to the minimum permitted by the exigencies of the finish and the structure of the fabric.

Calendering, beetling and chasing, but not, of course, drying upon the Palmer machine, reduce both cementation of yarns and fibres, and the stiffness of the cloth as determined by bending to some extent, but the resistance to alteration of the angle between warp and weft is increased, especially by calendering, this kind of set being termed " papery finish " commercially.

True breaking operations reduce resistance to all types of distortion and involve relative movement of the yarns, the fibres, or both.

The usual method involves rapid reversal of a short radius of curvature, by means of bars, knife edges, scrolls, or rollers studded with round projections (button breaker) ; only the latter is used upon crêpe fabrics, since this type of breaking depends essentially upon tension : the button breaker is in rolling contact with the fabric and therefore the tension is smaller.

The only completely tensionless process is that of the card-covered roller machine (Gessner) (see also Thickness, p. 871).

Faults.—The button-breaking process, if used upon fabrics showing a large extension at small loads, may cause a peculiar dappled appearance due to local removal of excess crimp by the thimbles, which causes a difference in the reflection of light. This effect is characteristic, and arises from no other operation ; it is best detected by examination in reflected light from a parallel beam.

Small sharply defined displacements of the weft in relation to the warp may arise from the needle breaker, if carelessly operated. Here again the effect is characteristic, the distance between two weft threads showing a periodical fluctuation where the wires have pierced the fabric.

4. Jig Stentering

Resistance to relative movements of the yarns is reduced almost exclusively by the process of jig stentering. This involves continuous changes in the angle at which warp and weft intersect during drying, and must be effected under tension.

Faults.—The principal and almost inevitable fault in jig stentered finishes is that mechanical imperfection of the machine and structural variations in the cloth prevent the distortion of the fabric to any great extent for 2 to 4 ins. from each selvedge. All soft finishes or finishes which, although stiff, require freedom of angular distortion (such as organdie and linen finishes) should be tested for variation by the bending test, and the specific distortion test described below.

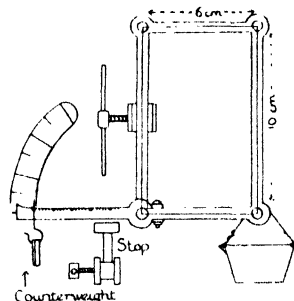
Testing of Softness

Softness implies reduction in stiffness and the deflection of a strip under gravity described in the section dealing with stiffness (p. 864) is applicable for this purpose. The free length of the strip is, of course, much less than with a stiffened finish. The test described below is based upon the jig stentering process, and measures the efficiency of that operation.

FIG. 141.

A strong rectangular framework (Fig. 141) with hinged corners 6×10 cm. between the axes of the hinges is used, fitted with fine needles projecting at right angles to the plane of the paper, every 5 mm. along the centre lines, to hold the samples; the needles at

the four corners should be 5 mm. longer than the intermediate needles, and the samples are first arranged by the corners, subsequently pushed upon the shorter needles.

The hinges should be quite free with a clearance between adjacent leaves and contain several leaves or distortion may occur. The girders are of deep channel section, into which the hinges are secured by bolts, or other suitable means. To one of the hinges is brazed a light beam notched to receive riders, and carrying a needle at the end positioned in line with the pivot centres; from the other end of the beam a light bucket of sheet iron is provided, to receive shot or mercury. For use the apparatus is clamped by the left-hand vertical beam, the counterbalance beam being horizontal: it is not necessary to counterbalance for the fabric, since the few grammes used has no influence upon the result. Strips of the fabric 7×11 cm. are cut from beside the selvedges and from the middle of the piece, mounted upon the

corner pins just taut, and pressed upon the supporting pins by a templet covered with layers of knitted fabric 2 cm. thick.

Shot is then run slowly into the bucket until the deflection of the beam reaches a pre-determined figure, which depends upon the free space available in the fabric for compression of the yarns. The type of fabric usually required to show freedom from resistance to distortion of this type is of open construction, and the weft can be turned 15° to 20° without tearing the fabric. Georgettes and similar fabrics offer little resistance to distortion and two or three samples may be superimposed in order to increase the load required.

While performing the test, local puckering may be observed due to local cementation: such places should be marked and examined after the test, since the effect usually results from gross local contamination with size or deposited impurities.

The test furnishes a useful indication of the presence or absence of cementation between warp and weft, but is of less service in measuring the draping properties of a fabric: for this purpose decrement of a horizontal vibration seems most nearly related to the commercially desired property, but so far as the writer is aware no apparatus for this test has been constructed. It is suggested that if two independently supported elastic beams are connected by a strip of fabric, the comparative response of the second beam constrained by the connecting strip, to forced oscillation of the first beam over a range of frequencies, will be characteristic of the elastic properties and internal freedom of relative motion of the fabric through which the motion is transmitted.

B. Stiffness

An increase in stiffness is incidental to many finishing operations which aim at other principal effects, and many methods which increase the stiffness alter the transmission and reflexion of radiation in a fundamental manner, to which reference is made in the appropriate sections (pp. 881-891).

During the last two decades stiffening processes have evolved from the simple addition of starch and inorganic fillers designed to give a semblance of substance to otherwise useless fabrics, to the deposition upon peptized fibres of filling substances which are demarcated by no interface from the original fibre, and are equally resistant to removal or degradation.

For commercial purposes stiff finishes may be divided into three categories :—

1. Permanent. 2. Semi-permanent. 3. Non-permanent.

The line of demarcation is purely arbitrary, and depends upon the difference in resistance to normal influences between the finished and

untreated fabrics. For example, protein formaldehyde finishes are quite as resistant to washing as wool if properly condensed, and must therefore be classed as permanent. On the other hand, the action of alkali will remove them from cellulosic fibres, hence the grade is reduced to semi-permanent.

A second instance is the variation in the same process. Urea-formaldehyde resin when properly applied is permanent, but the usual article of commerce can only be classed as semi-permanent in resistance to washing. For the purposes of the present classification it is assumed that all processes are executed by the best possible methods, and the usual causes of inferior results are indicated in the appropriate sections.

1. Permanent Finishes

A finish which will withstand substantially unchanged washing ten times for ten minutes in 1 per cent. sodium oleate (at 100° for cellulosic fibres, 80° for silk and cellulose acetate and 60° for wool) with intermediate drying, may be termed permanent.

The production of permanent stiffness usually involves the partial solution of cellulosic and cellulose acetate fibres, with or without the application of a binding agent which resists removal. This process gives the most permanent results when the peptized cellulose and the binding agent become flocculent under the same conditions, thus avoiding the formation of an interface. It is possible to obtain finishes of great permanence to washing when an interface is formed, but resistance to mechanical removal is less satisfactory.

Mercerization almost invariably precedes the permanent finishing of cellulosic fibres in order to improve the accessibility of the cellulose chains.

The most usual methods of stiffening being cheapest and most convenient consist in subsequently peptizing the cellulose in caustic soda saturated with zinc oxide at 10° or thereabouts, or in sulphuric acid (sp. gr. 1·55 to 1·65) at 12° or lower. The two types may be distinguished by the load extension curve, after relaxation in hot water, and drying on a wire tray. The sulphuric acid treatment fixes the dimensions and configuration of the fabric, thus reducing the extension; refrigerated caustic soda causes considerable shrinkage of the weft, and increases the extensibility after relaxation. A sulphuric acid finish frequently shows little or no viscose reaction, due to formaldehyde employed in the acid bath to diminish the rapidity of solution of cellulose.

Ammoniacal copper hydroxide is less frequently used, but it is largely employed for the application of cellulose in solution, when a permanent filling is required. Solutions of cellulose in refrigerated

caustic soda, sodium, zincate, sulphuric acid, or viscose are commercially employed for the same purpose. Unless residual sulphur or copper oxide are present, it is not possible to distinguish the products, since all deposit highly reactive cellulose upon the swollen fibre.

It is possible to produce stiffened finishes of merit by exposure of the alkali impregnated fabric to carbon disulphide, but so far as the writer is aware the process is not in use. The extension under load after relaxation is increased by this process, in much the same way as by refrigerated caustic soda.

Other binding agents in use for imparting additional stiffness to cellulosic fibres behave in much the same manner as regenerated cellulose, and include water-soluble methyl ethers of cellulose, and alkali-soluble glycol ethers. The fabric is impregnated in the aqueous or dilute caustic soda solutions respectively, and treated in 25 per cent. caustic soda solution, which precipitates both ethers. The methyl ether may be distinguished from the glycol ether by the resistance to removal by hot 3 per cent. caustic soda solution, in which glycol cellulose dissolves, but the cellulose applied in caustic soda solution (usually cellophane scrap) is almost equally soluble.

Stiffened finishes are obtained upon regenerated cellulose fabrics by analogous processes with greater ease, owing to the ready solubility of the cellulose in caustic soda solution or sulphuric acid. Fabrics so finished show poor tensile, rip and flexing tests, and find small application.

Synthetic Resin Finishes.—By far the greater part of synthetic resin stiffening is effected by urea-formaldehyde resins, since limitation of price, colour, odour, stability to alkali, and resistance to detergents rule out most other resins. The condensation, defects and testing are dealt with elsewhere (p. 873).

The methylene ether of polyvinyl alcohol (Formvar) is occasionally met with, and may be distinguished from methylolureas by its solubility in organic solvents and its resistance to aqueous acids. The polyvinyl ethyl ether, like most synthetic resins which are not condensed upon the fibre, or combined with a cellulose ester, is not resistant to emulsification by aqueous detergents.

Permanent stiffened finishes, which depend upon the application of esters or ethers of cellulose dissolved in organic solvents, are extensively produced, in plain effects and also in printed styles. Such finishes give a transparent, water-repellent film, resistant to soiling, and readily cleaned by sponging with water. The resistance to washing is good, but mechanical treatment ruptures the filling material, which is less permanently united to the fabric than when the swollen fibres are impregnated with a solution of cellulose or a derivative dispersed in the same or a similar swelling agent.

The most commonly employed ester is cellulose nitrate, which is relatively cheap and obtainable in many standardized degrees of degradation ; cellulose acetate is also employed in the production of more expensive goods. In addition to the cellulose nitrate, a plasticizer is added to prevent cracking, and a stabilizer which combines with the liberated nitric acid.

Faults.—In addition to defects due to the application of varying quantities of stiffening agent, which are readily estimated by extraction with cyclohexanone or other solvent, nitrocellulose finishes exhibit a variety of less readily detected faults.

The principal sources of damage are :—

Presence of Residual Solvent. The ester is frequently applied dissolved in an organic ester, which may also contain free hydroxy-groups in the acid or alcohol residues or in both. Such solvents are difficult to remove, and give rise to odours in storage ; such finishes should be heated over water (see p. 889) or subjected to steam distillation, and the distillate examined.

Instability of the Ester. Nitrocellulose hydrolyses slowly during storage, especially under the influence of light and moisture, to which action a water-repellent finish must exhibit high resistance. This hydrolysis is accelerated by the presence of residual solvents or other substances capable of associating with water, and should be counteracted by the addition of an unsaturated basic inhibitor such as is employed in the stabilization of nitro-explosives (p. 501). The writer has examined both printed nitrocellulose effects and plain finishes from which the inhibitor has been omitted, and found that the liberated nitric acid had destroyed the contiguous cellulose, during storage or use. The wet Fadeometer exposure described in the section on Wear (p. 929) is useful in estimating the liability to hydrolysis, but further information may be gained by extracting the test specimens with cyclohexanone, after the tensile determination, and testing for oxycellulose by any standard reduction method which the colour of the specimen permits. Intense degradation at the cellulose surface contiguous to the nitrocellulose may be observed, which would not be clearly shown by the tensile tests on thick fabrics.

Separation of the Plasticizer. An enormous variety of plasticizers is at present available, of which some are soluble in cellulose nitrate, others less so. The latter tend to separate from the ester in storage and when exposed to light, causing discontinuities in the film. The Fadeometer exposure will indicate the physical stability of the film in addition to the chemical stability. A further result of this defect, or of the use of excessive plasticizer, is loss by emulsification when treated with detergent. The finish is thereby rendered less permanent, while the stiffness and resistance to soiling are likewise diminished.

2. Semi-Permanent Stiffened Finishes

A semi-permanent stiffened finish is considerably affected by the washing tests above described (p. 865), but is not removed by boiling with water, or rendered adhesive by cold water. This definition corresponds to the commercial requirements of a finish less permanent and expensive than the permanent group, but which can be wet processed without injury.

The principal semi-permanent finishes are based upon normal stiffening agents which are combined with a substance or subject to a process to reduce the solubility in water.

The usual stiffening agents employed comprise three groups: carbohydrates, proteins and synthetic resins, but mixtures are of common occurrence.

Carbohydrates. The most common of all semi-permanent finishes is starch, usually farina, the swelling of which is reduced or inhibited by condensation upon the fibre with an aldehyde resin; diacetone-alcohol-formaldehyde resin is the best known and most permanent, but the cheaper urea-formaldehyde resins give useful results.

Like other finishes dependent upon the condensation of synthetic resins, commercial finishes rarely exhibit the resistance to washing which can be obtained by baking at a sufficiently high temperature. If thoroughly condensed the diacetone-alcohol-formaldehyde resins make the starch filling very resistant to soap, and if used for cementation processes the filling, being protected from mechanical removal, is permanent to the usual influences.

The proportion of resin to starch varies from 5 to 10 per cent., but an increased proportion, especially of the methylolurea resin, is sometimes employed. When properly condensed, the swelling power of the starch is much diminished and it does not show the blue coloration with iodine, but diastatic ferments are still effective in removing the finish.

The finishes are liable to the various defects enumerated in the section on Creasing (p. 873), but owing to the smaller proportion of resin present the development of free formaldehyde in storage seldom occurs.

A semi-permanent carbohydrate stiffening frequently employed is produced by impregnation of the fabric with the alkali-soluble extract of seaweed technically called alginic acid, which is rendered insoluble by the application of an aluminium salt. Treatment with acid extracts the aluminium, and the finishing agent may be extracted with ammonia.

Proteins. Albumin, gelatin, and casein condensed with formaldehyde upon the fibre are employed in the production of finishes, the best of which exhibit very high resistance to washing and to mechanical

removal. The protein finishes (among which gelatin is included on grounds of expediency) are not resistant to alkali and are readily hydrolysed by caustic soda. The finishes are not readily distinguishable; the presence of phosphate in the ash or caustic soda extract is not necessarily conclusive evidence of the presence of casein, since ammonium phosphate is sometimes used as a catalyst with hexamine, and the acid remains in the protein after washing. Owing to the cost of egg albumin it is rarely used.

Synthetic Resins. Many synthetic resins are employed in finishes which modify the stiffness either purposely or incidentally. Resistance to water is generally good, but the fatty character prevents absorption upon the fibre, and brings about loss by emulsification on washing.

The resins found in commerce include polystyrols, coumarones, common colophony, polyvinyl ethyl ether, and the lower esters of acrylic and methacrylic acids. The polyvinyl ethyl ether, acrylic esters, and methacrylic esters are not water repellent, and are not usually employed except for cemented interlinings, in which position the absence of circulation due to the surrounding layers of fabric prevents rapid loss by emulsification.

Solubility in alkali renders colophony readily distinguishable. The polystyrol and coumarone resins are very similar in most properties, being reversibly thermoplastic and resistant to acids and alkalis. Polystyrol resins are, however, colourless, and less brittle than coumarone resins, and are therefore preferred for textile purposes, if appreciable quantities are applied. So far as the writer is aware, colourless coumarone resins are not marketed, although described in patent specifications.

Testing.—In addition to the general tests for stiffened finishes, which are given at the end of the section, semi-permanent finishes are usually required to behave satisfactorily when subjected to some specific operation, involving immersion in water.

Test specimens are cut at the same time by means of a washer punch from several superimposed layers of the fabric. Each wad is then impaled upon a large needle, dipped in water at the stipulated temperature, and dried in an air-oven.

After drying the several layers of the wad are required to fall apart, and a well-baked finish shows no adhesive tendency.

The resistance to deflexion by small stresses which is increased by stiffening operations, involves the thickness and weight of the finished fabric, in addition to the distribution of the finishing agent with respect to the fabric and the continuity of the assembly layers. The simplest characteristic to measure is probably the length of a strip of the fabric, which, when suspended horizontally by one end, is deflected by a standard distance from the horizontal.

The apparatus required consists of a smooth plane surface (Fig. 142), for which five-ply board is satisfactory; to this is secured a small table, with a plane surface of vulcanite 2 ins. square. To the surface a piece of brass is attached by two pegs or screws floating vertically, but without horizontal freedom. A vertical board runs the length of the base; on it is drawn a reference line, the determined distance (conveniently 1 cm.) lower than the plane of the table.

The test specimens must not be creased or distorted, and if the goods are rolled or lapped, the samples should be allowed to relax in single fold upon a plane surface until the acquired curvature disappears. Test specimens (20×2 cms.) are then cut by the guillotine, placed flat along the base board, and one end carefully passed between the table and the weight. This end is slowly pulled by the left hand until the free end of the strip is raised from the base board to the reference line, and the length of the strip measured. Since the two sides of the fabric are rarely similar, alternate strips should be used face up and face down, but the same strip cannot be used twice.

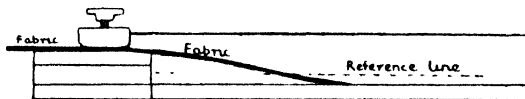



FIG. 142.

Difficulty frequently arises from the presence of discontinuities in the stiffness, which are caused by creasing of the fabric prior to finishing. An occasional defect of this type may not be serious in all cases, but the presence of several faulty places constitutes an objectionable defect, and for this reason the number of abnormal test pieces should be recorded.

Fabrics which are required to be water resistant can usefully be tested after desiccation, and after conditioning at 100 per cent. R.H. Apart from paraffin wax finishes complete agreement between the two tests is very rare, and indicates that even unsaturated hydrocarbon resins are permeable to absorbed moisture.

3. Non-permanent Finishes

Non-permanent finishes are more or less removed or rendered adhesive by boiling in water for five minutes.

For practical convenience this group may be divided into two classes, namely, filled finishes, which block the interstices of the fabric to a greater or lesser extent, and stiffened finishes, which depend upon the cementation of the fibres or filaments by a film of finishing agent.

The first type of finish is almost invariably based upon starch, to

which is added an inexpensive inorganic filler such as china clay, French chalk, "mineral white" (ground gypsum), or, if much weight increase is required, barium sulphate.

The second type of finish is in practice restricted by economic reasons to a few of the substances which might be used. If less than 2·5 per cent. of finishing agent is employed, locust bean mucilage, gelatine, alkaline extract of sea-weeds, gum tragacanth and degraded starch products are usually employed; for greater weight increases dextrins are almost universally used.

Stiffness Testing

In many cases a stiffened finish is required to possess resistance to mechanical disintegration. This is determined by the yield point on the load/extension curve; after the fabric has been extended the stiffness may again be determined. Sulphuric acid finishes are particularly resistant to extension, and the stiffness is not impaired by loading to the same extent as most finishes of this type.

Tensile and Ripping Strengths.—The resistance to tearing is necessarily reduced by stiffening operations, since the fibres and yarns are unable to adjust their orientation. The apparent strength of the finished goods is determined by the extent to which the yarns and fibres have been extended prior to fixation of the configuration, the plasticity of the stiffening agents, which is influenced by the R.H., the extent of penetration of the finish into the fabric and yarn interstices, the ratio of filling to fibre, and by any mechanical or physical degradation of the fibre. Permanent finishes must be incorporated as thoroughly as possible in the yarns, as must finishes aiming at improving the optical homogeneity of the fabric, and the reduction in tensile and ripping strengths is not appreciably affected by slight variations in the finishing process. Finishes which are applied to one side of the fabric only, give rise to considerable variations in the mechanical properties of the fabric, according to the extent to which the yarns have been penetrated and cemented by the stiffening agent.

The most effective method of controlling this factor is by examination of cross sections, but reduced ripping strength is the most serious result and the variation is such that the matter can scarcely be overlooked if the mechanical properties of the fabric are controlled.

C. Thickness

While the thickness of fabrics is easily ascertained by the micrometer, generally by measuring several layers under some arbitrary standard of compression, the expert buyer of fabrics will often say that this or that cloth feels thick or thin. When such a statement is

made it is seldom confirmed by actual measurement of thickness even when the buyer says that one piece, nominally the same fabric, is thick compared with another. There is perhaps some character of resilience, smoothness or suppleness which gives the impression of thickness or thinness.

Apart from processes which increase the thickness of the fabric incidentally, by permitting the spinning strains to relax, with consequent contraction in length and increase in diameter of the yarns, certain operations of finishing aim specifically at increasing the volume occupied by the yarns ; the group comprises decatizing, raising and " Gessnering," the last mentioned being named after the manufacturers of the machine.

Decatizing consists in blowing apart the fibres composing the yarn by means of steam jets. In addition to the fundamental purpose, the process is frequently employed to impart a temporary set to fabrics, thus inhibiting shrinkage during storing. The changes produced by decatizing are by no means marked : the efficiency of the operation may be judged by examination of the apparent thickness of several superimposed layers of the fabric under very small compression.

Raising consists in scratching the surface of the fabric by means of wire-card ; according to the staple length, twist, and coefficient of friction the fibres with which the wires engage may be drawn from the yarn, or broken. Hence the process is liable to cause very serious loss in tensile strength, and goods which have been subjected to this operation should be tested regularly, and several samples examined from each batch, since the extent to which the wire-cards penetrate the fabric may vary within a short distance.

Testing. The effect of raising invariably diminishes the tensile and ripping strengths, and the more thorough the raising the greater is the loss. For this reason a standard strength loss must be fixed for each fabric and finish ; in the absence of an agreed standard it is not possible to assess a result as satisfactory or otherwise. The object of raising is to increase the volume of the fabric, thus reducing the transmission of heat.

Since the human body is usually the object losing heat, the kata-thermometer may be employed to test the effect of the operation, or E. Müller's apparatus based on the same principle (H. Keyl, Dresden). Alternatively, the thickness of the fabric may be measured, using a micrometer, or, if more detailed information is desired, the compression-load curve of several superimposed layers.

Gessnering.—This operation consists in running the fabric in rolling contact with wire-card covered rollers. Unlike the raising machine, the Gessner apparatus does not rupture or tear out the fibres, the increase in volume being obtained by simple displacement

of the fibres above the original yarn surface. It is not therefore necessary to control the tensile strength of fabrics finished by this process, a measurement of the thickness being sufficient to determine the efficiency of the operation.

D. Resistance to Creasing

The resistance to creasing of cellulosic fibres is frequently improved either permanently by condensing formaldehyde with the cellulose, with or without a third substance capable of reaction with formaldehyde, and absorption upon cellulose; or non-permanently, by baking the cellulose after impregnation with boric acid and a suitable catalyst, usually calcium acetate.

Permanent crease-resisting finishes exhibit reduced elastic hysteresis, and similarly diminished capacity for hydration, swelling and peptization in aqueous media. Usually formaldehyde and urea are thermally condensed with cellulose in presence of an acid catalyst.

Faults.—Faults which arise from these finishing operations are :—

(1) Uneven condensation due to variation in temperature during baking treatment. Usually the middle of the piece is less completely condensed than the edges, but the effect is reversed if the fabric is incompletely dried along the edges prior to baking. The incompletely condensed areas exhibit diminished recovery from creasing, greater affinity for direct dyestuffs, and a reduced content of formaldehyde and other reagents after washing; prior to washing, analysis may show a greater content of reagents due to the smaller loss of volatile bodies. Frequently the shade of the fabric varies with the degree of condensation.

(2) Lack of permanence, due to inadequate baking, or too little catalyst. Very rarely an unsatisfactory effect may be due to hydrolysis of the condensation products by inorganic acid catalyst (ammonium phosphate) resulting from exposure to temperatures above 150°.

3. Cementation of the fibres may be caused by premature polymerization of the impregnating bath, by the use of too strong an impregnating bath, or by migration of the resin to the surface during drying. The cementation, which is visible under the microscope, results in undue stiffness, brittleness, a milky appearance, and much diminished resistance to abrasion. Finishes which have been faulty in this respect are frequently treated with lubricants, and softened mechanically in order to disguise the fault. Wear and tensile tests upon crease-resistant finishes should be executed upon samples washed for ten minutes in a boiling solution containing 2·5 g. Emulphor EL, 0·5 g. Igepon T conc. and 0·5 g. Calgon (unbuffered) in 100 ml.

water, then rinsed in hot water several times to remove traces of fatty matters, and dried upon a wire tray.

4. Development of odours during storage. This is commonly due to insufficient soaping (odour of formaldehyde); more rarely, to the presence of softening agents, or methylene ureas formed during condensation, which evolve alkylamines on oxidation. Fabrics are frequently found to have missed the washing process after baking; such goods contain the acid catalyst, in addition to uncondensed alkylolureas, and absorbed paraform; the aqueous extract from crease-resistant samples should show no trace of acid, or of alkali, since the former shows inadequate washing, and the latter promotes the photocatalytic reduction of some dyestuffs by the resin.

5. Resins containing formaldehyde and especially urea-formaldehyde products are capable of oxidation at a very rapid rate in favourable circumstances. For this reason some dyestuffs, especially those containing azoic linkages, are so rapidly reduced in the presence of resins, when acted upon by light, that destruction of the dyestuff may be complete after exposure to sunlight for half an hour. Conversely, dyestuffs readily oxidized photocatalytically are usually protected by the resin, which is oxidized preferentially. It is therefore necessary to examine the influence of resin finishes upon the light fastness of dyestuffs irrespective of the fastness or otherwise of the untreated dyeings.

Testing. Owing to the fundamental changes brought about by condensation with resins at high temperatures, goods which have been finished in this manner require careful examination, since small variations in the process may give rise to serious defects. No correlation necessarily exists between the resin content and resistance to creasing, but variation in the resin content after washing may indicate variable condensation conditions, which give rise to scattered recovery results and to evolution of formaldehyde during storage. The slow moisture regain of fabrics which have been treated at high temperatures makes careful conditioning a necessary preliminary to all physical tests.

Tests for Resistance to Creasing.—No means of testing has yet been devised to measure resistance to creasing in terms which give complete agreement with the judgment of an expert handling the fabrics. This is not surprising in view of the requirements of those buyers who really know how satisfactory some crease-resisting fabrics may be, and also know the possible defects. Although a fabric may resist creasing very well indeed, whether judged by any method of measurement or by expert handling, it may have undue harshness or hardness, or it may drape badly when made up into a garment owing to an excessive degree of resistance to creasing. In this latter character the fabric tends to behave in some degree like sheet rubber.

The usual " recovery test " which measures the degree to which a fabric recovers from, or flattens after, creasing, is one of very great practical utility, but it is better regarded as a good sorting test than as an accurate means of measuring resistance to creasing.

The Recovery Test. Conditioned strips of fabric measuring 4×1 cm. are cut both warp and weft way from different parts of the sample, avoiding proximity to the selvedge. Each strip is folded with the crease across the middle, laid upon a flat surface and subjected to a weight of 200 g. for three minutes. The creased strip is then straddled over a thin horizontal wire and allowed five minutes to " recover " before measuring the distance between the two ends. The test is quite an arbitrary one and admits, of course, of many refinements, such as standardization of the shape or of the weight, taking a vertical reading of distance between the two ends with scale and mirror to avoid parallax, and flotation of the creased strip on mercury, instead of suspension on the wire, to avoid bending of the ends due to gravity. The crease may be kept under pressure of the weight for many hours and similar time may be allowed for recovery. The result is expressed direct in cm.

While the test is generally fairly reliable for comparing samples of the same fabric treated under different conditions, it can hardly be expected to allow of close comparison being made between fabrics of different weave structure or made from different kinds of fibre or yarn. Fabrics before treatment by a crease-resisting process naturally yield very different results owing to difference in structure, but the application of the treatment always produces a very marked difference, provided that the treatment follows the usual course, the treated material commonly giving from 2·7 to 3·2 cm. as the result of the short period test. Estimation of the amount of " resin " in fabrics containing formaldehyde condensates may be performed by extraction in 10 per cent. hydrochloric acid at 80°, followed by very thorough washing. Formaldehyde may be estimated by the well-known Schryver's test.

Fastness to Washing. Cut a yard of material in strips 6 ins. wide, parallel with the weft; determine the loss shown by three alternate strips after rinsing for three minutes in 0·25 per cent. Na_2CO_3, which provides a reliable indication of the thoroughness of washing after condensation. Determine the further loss in weight after extraction for twenty minutes at the boil, with 1 per cent. sodium oleate and 0·5 per cent. sodium carbonate; this indicates the resistance of the finish to washing.

Estimation of Resin Content. Methylolurea resins may be extracted with 10 per cent. mineral acid at 80°, or with 10 per cent. lactic acid at the boil; if other determinations are to be made upon

the extracted material, the extraction bath should be renewed continuously if possible, in order to avoid formation of methylene cellulose, or alternatively a primary aromatic amine may be employed to remove the formaldehyde as liberated. Resin should be determined on the soaped and unsoaped strips, taking the sides and middle of the fabric separately, since variation frequently occurs.

Recovery from Creasing. This should be determined for unsoaped and soaped samples, taking strips at intervals across the piece. The strips should condition for a day prior to testing.

Free Formaldehyde. This may be determined approximately by colorimetric methods using Schiff's Reagent, morphine sulphate, or phloroglucinol: the last named appears to be the most reliable. Since, however, the resin is never perfectly stable, but tends to hydrolyse, the determination should be supplemented by examination of the behaviour on storage. The resistance to soaping gives an indication of the degree of condensation.

Stability. The resins and softening agents containing alkylamine residues may give rise to offensive odours in storage. As an accelerated storage test a loose roll of the fabric should be placed over water in a stoppered vessel at 60° for a few days, and the odour observed. Free acid and alkali should be determined. The former is usually present as tartaric or phosphoric acids.

Tensile Strength: Ripping Strength. The influence of condensation with formaldehyde resins upon tensile strength is relatively small in animal fibres. Cellulosic fibres exhibit a reduction in tensile strength and ripping tests roughly proportional to the degree of order in which the units are arranged. Extraction of the resin restores the original properties, provided that no appreciable amount of methylene cellulose is present. This may be judged by diminution in affinity for direct dyestuffs, or by the slowing of the viscose reaction.

Unfixed fatty matter should be removed prior to testing.

Load Elongation. Resin finishes may diminish the elongation very considerably when cementation occurs, tensile and ripping strengths, and wear resistance also being affected.

E. Adhesion

The ability of two fabrics to cling together owing to interlocking of surface hairs constitutes a defect in most fabrics, and an advantageous property in fabrics which are to be bonded in layers. All operations which smooth the surface of a fabric reduce the clinging power, whilst raising and increasing the apparent thickness by the Gessner machine, and Dekatizing (see p. 872) increase the property.

The cohesion between two folds of the same fabric is usually in

question, since the clinging of a garment cloth is not permissible. In such a case the defect is also governed by the weight and elasticity of the fabric, and is not a simple function of the work involved in separating two surfaces. Occasionally the property has proved decisive in causing the commercial failure of a fabric, and is therefore of much economic importance, but is very difficult to evaluate. The following test is not sufficiently accurate to yield more than a rough indication of clinging power, which varies from place to place in an erratic manner, but will distinguish between fabrics which are satisfactory, doubtful and bad in this respect.

Test strips are cut diagonally with a guillotine, 9×1 in., three strips being required for each test. One strip, AA, is arranged face

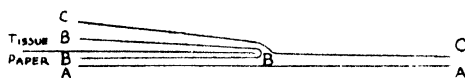



FIG. 143.

up, on a plane surface, the second strip, BB, is carefully placed face downward upon AA and folded back upon itself, the reverse sides being prevented from clinging by insertion of tissue paper, and the third strip, CC, is placed face downward covering half of B and half of A (Fig. 143). Other test specimens are assembled similarly, arranged with double and single ends alternately, in order to obtain even thickness, and the whole placed beneath a clamping board, which is loaded with weights to 5 lb. per square inch, and left for one hour.

The specimens are then examined as follows: Each test specimen of three pieces is carefully removed, the tissue-paper withdrawn from between BBB, and the ends BC clamped in a single jaw, vertically above the middle point of the specimen. The clamp is then raised slowly and vertically with uniform speed from the plane of AA. At first the three strips separate from the middle point, but as the lengths in contact diminish and the catenaries increase, a point may be reached at which A no longer separates readily from B and C but follows B and C, to form a triple catenary, if the fabric clings (Fig. 144). Most

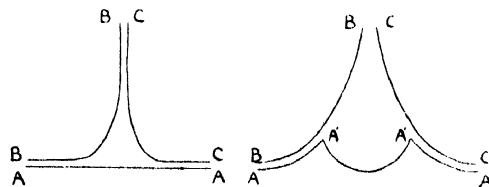



FIG. 144.

fabrics separate completely, the clinging power being negligible, in others AA′ may be 1 in., but occasionally a fabric is tested which

usually combines light weight, low twist, and short staple, and scarcely shows any separation : such fabrics are useless for dress purposes, but conversely give remarkably good adhesion when cemented to form multiplex fabrics.

Multiplex Fabrics

The possibility of combining several properties in one assembly by cementing together two or more layers has become an important branch of the textile finishing industry. In contradistinction to dress materials, fabrics for cementation require a high clinging power to act as reinforcement of the actual bonding agent, and projecting surface hairs are not removed, but are increased in number by processes which involve scratching or sticking with needles, blowing with jets of steam, or raising by electrostatic forces.

Estimation of the amount of nap is most readily accomplished by measuring the thickness of several superimposed layers of fabric under increasing load, but a standard of comparison is necessary. If a standard reference is not available, the nap may be removed by singeing with a bunsen burner until the surface is clear, after which the thickness-compression curve is again examined.

Experiment has shown that the force required to tear apart two cemented layers of fabric may be increased 30 per cent. by the presence of raised fibres upon one of the cemented surfaces : in case of variation in adhesion between two fabrics this factor must therefore be examined.

The variation may occur in the face cloths, the interlinings, or in both, and will not be apparent in the case of coated interlinings until the adhesive has been extracted.

Adhesive Interlinings

The preparation of adhesive interlinings used in the manufacture of three-ply collars, cuffs, etc., is a comparatively recent development. The interlinings are of two types : one (Trubenizing lining) contains threads of cellulose acetate, which is rendered plastic by heat and organic solvents during the bonding ; the second type consists of an ordinary fabric superficially coated either completely or in a printed pattern, with an adhesive which may be thermoplastic, or may need organic solvents.

The bonding process involves several variables, consequently it is necessary to test the interlining in the precise conditions in which it is to be utilized, since a lining may be very satisfactory in one set of conditions and fail completely if one variable is altered.

(a) *Linings containing Cellulose Acetate Yarns*

1. **Displacement of the Cellulose Acetate Threads.**—The efficiency of the interlining depends upon the amount of ester thread present upon the surface of the interlining. Mechanical pressure embeds the weak and plastic ester fibre into the cotton or wool yarns, into which it diffuses during bonding, and therefore is not available for cementing the interface.

This defect reduces the adhesion at a given pressure during bonding, but increased pressure while the cellulose acetate is dissolved drives the solution to the surface; the best result at any pressure is, however, lower than the maximum adhesion of a perfect lining. The extent of the displacement may be estimated either by dissecting the fabric and examining the form of the acetate threads, or by dyeing the fabric and a standard with Cellitone Black in the same bath, after which the difference in the exposed area may be estimated from a photomicrograph.

2. **Hydrolysis.**—This is liable to occur in two forms: a general saponification of the whole surface, due to treatment in alkaline liquors, and a very drastic saponification confined to a few filaments at points where the acetate yarn projects. The general effect of this fault is similar to that described in the first paragraph, but may be distinguished by the fact that improved adhesion is obtained when the time of fusion is prolonged, as a result of the retarded solution of the filaments, and the hydrolysed areas become dyed with Diamine Sky Blue FF in a depth proportional to the degree of saponification.

The variation in adhesive power due to slight hydrolysis is conveniently followed by suspending a strand of the acetate yarn vertically in acetone, and noting the number of seconds which elapses until the specimen becomes fluid. Times may vary from five or six seconds upwards, and should not exceed sixteen seconds; if, however, the yarn is spun with a delustrant, the time of solution is slightly longer than that of the corresponding bright quality.

This test is very useful in the routine examination of cellulose acetate yarns and fabrics, since the rate of solution is very sensitive to degrees of hydrolysis scarcely detectable by analysis, and to the presence of undesirable surface films.

3. **Extension of the Fabric.**—The method by which cellulose acetate adhesive linings are bleached may give rise to undue extension in the direction of the warp, such goods should be tested regularly for liability to shrinkage and variation in crimp.

(b) *Linings coated with Adhesives*

These may be subdivided into two groups :—

1. Water resistant and soluble in organic solvents. Plasticized cellulose acetate, methyl and methylene polyvinyl ethers. Polyvinyl esters of fatty acids containing five or more carbon atoms.
2. Adhesion destroyed by water, but soluble in organic solvents. Methyl and ethyl esters of acrylic and alkylacrylic acids and polyvinyl acetates.

Faults.—1. The chief faults which arise from this finish, which is a special case of stiffening, are insufficient adhesive, or maldistribution of adhesive. Where variation is suspected the adhesive may be dyed with a cellulose acetate dyestuff, and the distribution examined microscopically. As in the case of interlinings woven with cellulose acetate the distribution of the adhesive is more important than the quantity contained in the fabric, especially since the present group of interlinings is usually bonded with heat alone, in the absence of solvent.

2. Defective bonding may result from the use of too little plasticizer in the adhesive ; tests carried out at different bonding temperatures will show the magnitude of the variation. Conversely, if too much plasticizer is used the bonding temperature is lowered, but the resistance of the adhesive to removal by washing is usually reduced, since plasticizers are usually readily emulsified esters.

Testing.—A number of strips, which may conveniently be 6×1 in., is cut from various places across the piece, and bonded back and face to larger pieces of the same facing fabric ; since the bonding is liable to vary, not fewer than three separate strips should be used from each 12 in. across the sample. After bonding the test pieces are placed in a load-extension tester, one jaw of which holds one thickness of facing cloth, the other one thickness of facing cloth and the interlining, and the mean load noted at which the face cloth is steadily torn from the interlining. The specimen should not be ripped past the half length. The test piece is then reversed in the jaws, the second face cloth being torn from the interlining in a similar manner, starting from the other end of the specimen. One side of the interlining usually shows better adhesion than the other, and the mean is customarily used : the lower figure should exceed $2\frac{1}{2}$ lb. per inch width of interlining, and the mean 3 lb. per inch, but much higher results are obtainable if the face cloths are suitably finished.

It may be noted that the presence of size on the interlining seems to have little influence upon the adhesion, and the figures for carefully purified interlinings differ little from those given by cloth from the loom.

Estimation of Adhesive.—All adhesives employed for fused interlinings are extracted by cyclohexanone, which has the additional property of evaporating completely from the residue after distillation. The wax is also extracted from the fibre and from the size of unbleached fabrics, but since the determinations are usually comparative the error has little influence.

Fabrics containing cellulose acetate may be extracted with toluene or petroleum ether, prior to extraction of the ester, but coatings of cellulose acetate may contain hydrocarbon soluble plasticizers. For this reason the determination is only of comparative value. The same remark applies to estimations of the acetyl content of coatings by hydrolysis with caustic soda and determination of the acid split off, since plasticizers may seriously affect this value.

F. Transmission of Light

Improved transmission of light is commonly produced by increasing the transparency (optical continuity) of the yarns by tension while the fibres or filaments are superficially plastic, thus improving the parallelism with the axis of the yarn, by filling the interstitial spaces of the fabric with a transparent medium, and then compacting the result by pressure or heat, or by a combination of both methods. If a filling medium is present, friction is usually employed in addition to pressure, in order to improve the smoothness of the surface and the flow of the filling. The methods employed increase the rigidity of the fabric, and differ from those of stiffening only in the choice of optically homogeneous filling media, and in the almost invariable use of a compacting process, to facilitate which a plasticizer is customarily added. The degrees of permanence are similar to those described in the section on Stiffness (p. 864), ranging from simple calendering finishes upon soluble starch filling, to deposits of cellulose or cellulose esters almost inseparable from the original material.

Unassisted Transparent Finishes

These are produced almost exclusively by alternate treatment in sulphuric acid and caustic soda, and are little affected by mechanical distortion or elongation, since the warp and weft configuration has been stabilized under tension and is therefore little changed by subsequent stresses.

Greater transparency is obtained by superficial etherification of the fibre by condensation with ethylene oxide or glycide, and subsequently compacting as usual. Samples of these finishes have been met with, although it is unlikely that so costly a process can become commonly applied. The fibres are not permanently cemented together in the

transparent areas, and separate when the fabric is distorted. In comparison with processes dependent on solution of unmodified cellulose these finishes show increased imbibition in water and, in 5 per cent. solutions of caustic soda, lower elastic moduli, together with increased extensibility with marked hysteresis loops.

Faults.—The requirements of a transparent finish devoid of filling differ somewhat from those of a filled transparent finish. In addition to the improved general transparency, it is essential that the spaces between the yarns should be regular in size, as large as possible, and free from obstructions.

1. *Variation* in the size of interstices will be indicated by a variation in transparency and rigidity across the piece. Usually the transparency is smaller and the stiffness greater in the neighbourhood of the selvedges than in the middle of the fabric, and the quantity is capable of measurement by generally applicable methods.

2. *Obstruction* of the interstices can in theory be measured by counting the percentage of filled spacings in sufficient samples, but the labour involved is impossibly great, owing to the variable incidence of the fault, and only visual comparison is practicable. The defect may arise from the presence either of protruding hairs or of degraded cellulose or both, and since no standard can be prescribed it is not possible to attribute the fault to either source without a comprehensive examination of the fabric and the constituent yarns. An unsuitable fabric will not yield satisfactory results by commercially practicable methods, whilst the best fabric may be ruined by unsuitable processing.

Protruding hairs may be classified according to origin as an inherent property of the fabric, or as an acquired property due to faulty finishing processes. Inherent hairiness may be due to coarse yarns, fibre of high hair weight per cm., short staple, or too close a construction of the fabric, which impedes the access of the singeing flame. Acquired hairiness may be due to defective or unsuitable (plate) singeing, mechanical rupture of the fibre (discriminated by Congo Red Test, p. 670) or chemical degradation of the fibre (shown by low viscosity figure, p. 728).

In addition to the obstruction of interstices by protruding hairs, a film of deposited cellulose may be responsible for the " window pane " effect. The rate of solution of cellulose in sulphuric acid is very sensitive to diminution in the micellar size, and if the viscosity is reduced during bleaching, the too rapid dissolution of the surface layer is not ordinarily avoidable, and a layer of parchment forms at the surface of the yarns and in the interstices of the fabric.

A special case of increased transmission of radiation which is more specifically a diminished dispersion of incident light is the treatment

of delustred cellulose acetate fabrics to restore in some measure the original optically homogeneous character. The delustring may be effected by boiling in a soap bath with or without a phenol, or by the deposition of urea or urea-formaldehyde resin upon the surface ; the relustring may be effected in the first case by the use of pressure and heat, which reduces to some extent the dispersion of light at the surface of the filaments, by applying a cellulose acetate solvent, or by applying a solvent together with an organic acid.

Delustring tends to reduce the tensile strength of cellulose acetate, especially if phenol is used, whilst the relustring may cause a further decrease, most marked when hot embossing is employed to restore the lustre. This weakening is most marked at the edges of the embossed or printed design, and may vary considerably from one selvedge to the other, since the effect is very sensitive to the pressure of the embossing roller. Such goods must therefore be tested for tensile strength in several places across the whole width of the sample.

Somewhat analogous is the process of increasing the transparency of cellulosic materials by local treatment with solvents, such as zinc chloride or calcium thiocyanate in which cellulose or cellulose esters and ethers may be dissolved. The effect of the salts is not very marked, and an addition of formaldehyde is usually made, in accordance with the original findings of Cross and Bevan, to increase the solubility. The effect is similar to that produced by sulphuric acid in appearance, and is quite reliable, but it is advisable to test the tensile strength of strips which include the printed areas, since the salts are liable to cause degradation of the cellulose.

The use of zinc chloride or calcium thiocyanate in the production of plain finishes has been tried on the commercial scale, but the smaller activity and greater expense of the peptizing solution, compared with sulphuric acid, has not permitted the extensive use of the process.

Assisted Finishes

Transparent finishes containing a binding medium are subject to the defects enumerated in the section dealing with Stiffness (p. 864), but the presence of local injury to the continuity of the finish is correspondingly more important ; visual inspection is, of course, possible in this case. Well-swollen starch is the usual basis of non-permanent transparent finishes, but often insufficient attention is given to reduction of adhesion in damp conditions, and to the lack of resistance to breakdown when tension is applied to the weft. The latter defect is also found in finishes with more pretensions to permanence. (See also adhesive interlinings, p. 878.)

The semi-permanent and permanent finishes are usually prepared

to exhibit resistance to definite influences, such as water-spotting or dielectric breakdown, and are produced with paraffin wax, nitrocellulose, polystyryl and polyvinyl resins, methyl and glycol celluloses, cellulose glycollic acid ether, more rarely, benzyl ether, and the benzoyl and acetyl esters. Esters of inorganic acids, usually phosphates, may be expected to occur, and oxalates are becoming more popular.

Testing

Transparency. This may be estimated visually or by using a photometric method. Effects which depend upon difference in transmission and dispersion between adjacent areas, require comparison of the intensity distribution of a reflected beam from each area, since one effect or the other is usually obtained by printing, and therefore superficial to some extent.

Stiffness test is described in the appropriate section (p. 864).

Resistance to Water. The resistance to dissolution by water may be estimated by the method described for permanent finishes (p. 865). This property has not received attention commensurate with its importance to users of tracing cloths.

Resistance to Elongation. The specimen is very slowly loaded on a load extension tester, and the point observed at which the specimen becomes optically heterogeneous. It is advisable to clamp a second specimen beside the one which is being tested, for purposes of comparison. It is usually found that the warp extension is small, and the load at which the structure breaks down correspondingly high, but the resistance to extension of the weft is frequently low.

Permeability. This is quite distinct from liability to solution in water, and may be measured by estimating by any suitable method (*e.g.* electrical conductivity or solution of dry dyestuff in contact with the surface) the time required at a given temperature by water or a salt solution to penetrate the fabric.

In some fabrics the receptivity for ink must be measured, and since diffusion takes place more rapidly through the interior of the fabric than through the surface layers, the time of diffusion through the whole of the fabric is not necessarily characteristic of the absorbency of the face side. In such cases the face of the fabric is covered locally with a standard ink, the excess removed after five seconds by blotting paper, and the depth of colour compared with a standard. The ink used should contain a soluble dyestuff which does not change in shade after drying or, like Alkali Blue, exhibit selective total reflection, and the temperature at which the test is made kept as constant as possible: variations in the conditioning of the fabric

affect the result more than changes in the surface tension and viscosity of the ink due to alteration in temperature.

G. Increased Specular Reflection (Lustring)

1. Swelling Treatments

This type of finish involves the swelling of cellulosic fibres and occasionally of wool, in aqueous caustic soda under tension. The preliminary swelling of cellulose may be carried further by means of ammoniacal copper hydroxide, carbon disulphide, ethylene oxide or glycide, and successive or simultaneous absorption of cellulose, dispersed in aqueous caustic soda or ammoniacal copper hydroxide, viscose, and water or alkali soluble ethers may be arranged. These further treatments result in cementation of the fibres, and consequent increase in stiffness, for which purpose they are commonly employed.

Chlorinated wool exhibits more regular reflexion than unchlorinated, among other properties: the faults arising are discussed under Shrinking (p. 899).

Faults.—**(a) Cotton.** (i) *Lack of Lustre.* The most common fault in mercerized cotton goods is inadequate swelling of the fibre, resulting in less perfectly elliptical cross-sections. Much commercial mercerization is nominal, the usual causes being inadequate wetting of the fibre, too short a time of swelling, too high a temperature of the mercerizing bath, or the presence therein of impurities which by absorption of alkali, or by dehydration, reduce the effective strength of the bath.

The apparent lustre of the yarns may also be reduced by the presence of extraneous matter, usually organic matter precipitated by calcium hydroxide. Such deposits may be removed by boiling in a solution of Calgon for a few minutes, while dullness due to inadequate swelling is not removed.

The increased regularity of the fibre surfaces is effectively displayed only when the arrangement of the fibres in the yarn is orderly; if sufficient tension is not applied during mercerization, the fibres will not lie parallel, and the lustre may be inadequate, although the cross-section is satisfactory. For this reason the determination of lustre in reflected light is a more reliable commercial criterion of efficient mercerization than examination of the cross-section. Tension is usually reduced in order to avoid possible damage arising from reduction in tensile strength, or excessive stretching of the warp in preliminary processes. If, therefore, the lustre is unsatisfactory after treatment for removal of deposits and despite satisfactory swelling of the fibres, tensile strength and shrinkage on washing should be tested.

(ii) *Stiffness.* Undue stiffness in mercerized cotton fabrics is frequently noticed. This property is controlled by the bleaching process, and may arise from degradation of the cellulose, or from very efficient removal of fat. Either cause is usually masked in subsequent treatment, and the most characteristic criteria are the reduction in thickness of the fabric in comparison with the normal goods, and the reduction in ripping strength after the removal of lubricants which are employed to conceal the condition, preferably by extraction with pyridine.

Wool.—The most usual fault due to the mercerization of wool is undue loss in tensile strength resulting from too weak an impregnating bath, to inadequate neutralization, or the use of too high a temperature.

Superficial deposits of calcium compounds may occur, as upon cotton. Mercerized wool is appreciably more lustrous than the untreated fibre and appears translucent under the microscope, like chlorinated wool, but is less harsh in finish than unmercerized or chlorinated wool.

The most common fault is diminished tensile strength, especially in the wet state, due to insufficiently rapid neutralization of the alkali; but too high a temperature of the impregnation bath or too low concentration of alkali have similar effects. In the usual conditions of operation, depletion of the alkali and acid baths may occur, and it is advisable to examine the wet strength of processed goods as a matter of routine.

Linen.—In the case of linen the increase of lustre obtainable by mercerization is not very great, and the principal effect is to increase the absorbing power of the cellulose and the compactness of the yarns, thus diminishing the disintegration which normally occurs in wear.

Stiffness due to mercerization is more pronounced, and if a supple fabric is mercerized it is essential to control the preparatory processes with care; the solubility number should be checked at all stages.

Degradation may result from the practice of allowing linen to lie about after mercerization with the alkali incompletely removed, since flax is less resistant than cotton to oxidation in these conditions, and the tensile test results show wide scattering, as the oxidation is very irregularly distributed.

2. Polishing Treatments

The regularity of the yarn surfaces is modified by operations which involve a rolling movement of the yarns. The operations include beetling, chasing, calendering with very soft bowls, and, to a lesser extent, jig stentering. The permanence of the effects may be enhanced by the use of glycol and methyl cellulose, synthetic resins or protein-aldehyde condensed on the fibre.

Faults.—1. The most common defect in connection with such finishes is inadequate previous purification of the fabric. In order to improve the regularity of the yarn it is necessary that protruding fibres be so displaced as to remain within the envelope of the desired yarn surface. Unless the static coefficient of friction between the fibres exceeds the coefficient of restitution for the new configuration, the effect of these treatments is not sufficiently thorough, and, moreover, diminishes rapidly in any subsequent operation. A small fat content, not exceeding ·03 per cent., is necessary for the production of effects which exhibit reasonable permanence.

2. Occasionally the fabric may exhibit an embossed effect, due to excessive local pressure from creases, sewings, or a second layer of fabric. The form of the fault will indicate the mechanical origin, but the permanent set is usually accentuated by a plastic condition of the fabric during the operation, due to excessive or uneven moisture content.

Testing.—When a standard of comparison is available, the samples may be compared in reflected light from a parallel beam visually or photographically; a good finish of this type should show little alteration in lustre after relaxation in boiling water for five minutes. When no standard of comparison is available, the surface regularity and smoothness of the individual warp and weft threads viewed against a contrasting background form a useful guide to the efficiency of the treatment, provided the observer is familiar with the general appearance of yarns of a similar quality.

Alternatively, the fabric may be relaxed twice in a boiling bath containing approximately 0·5 per cent. Emulphor EL and 0·5 per cent. sodium oleate for five minutes, being dried in hot air, without rinsing, after the first relaxation. An inherently lustrous fabric will remain substantially unchanged, whilst mechanically generated lustre will be largely eliminated.

3. Flattening and Embossing Treatments

The use of devices which press perpendicularly upon the fabric in order to form a plane surface is readily detected by visual examination. The most highly glazed finishes are produced by friction in addition to pressure; such finishes almost invariably include the use of a soluble starch preparation, gum, or low mol. wt. dextrine, in order to fix the set of the fibres. The thickness of the fabric is much reduced by these operations.

Faults.—The usual imperfections found in such finishes are:—

1. Irregularities in glaze repeated at regular intervals, due to uneven pressure surfaces.

2. Variation in the glaze from the neighbourhood of the selvedges to the middle of the piece, due to uneven impregnation or drying, prior to glazing.

3. Disintegration of the fibres at yarn intersections, due to excessive pressure, too high a coefficient of friction between the fibres, degradation of the fibre prior to glazing, and, in the case of regenerated cellulose fibres, insufficient drying prior to the treatment.

4. In highly friction calendered finishes the specular reflection is sometimes reduced by the presence of discrete particles of filling, usually starch granules, which increase dispersion of the reflected light.

Testing.—When a standard of comparison is available the distribution of a reflected beam may be compared photometrically. A complete analysis of a fabric in respect of its light-reflecting character, could only be achieved by plotting a complicated graph or series of graphs showing the intensity of reflected light at all angles to the plane of the fabric for all angles of incidence of the beam. Even then the analysis would not be complete, *e.g.* " watered " finishes where the reflection varies from place to place.

A modified specular reflection is obtained by embossing the surface of the fabric with a series of parallel lines, making an acute angle with the weft (Schreiner finish) spaced at intervals on the border of visual perception. The planes so formed reflect incident light in a series of narrow pencils. The effect is readily visible under the microscope in reflected light, and apart from the interrupted character of the reflected beam is similar in principle to a glazed finish. Owing to the great pressure and the cutting effect of the embossing roller, the tensile strength of Schreiner-finished fabric should invariably be tested.

H. Dispersion of Light (Delustring)

The dispersion of light at the surface of a fabric is increased by the deposition of discrete particles, or spongy surface films. The interior of the filament of cellulose acetate fibres is made discontinuous by treatment in boiling solutions of soap, to which may be added phenols, or cyclic alcohols or similar substances of which the molecules form a non-wetting surface when the hydrophilic groups are associated.

Many substances have been suggested for the modification of dispersion, but few have attained commercial importance, owing to difficulties in ensuring the regularity of the result.

The types of finish may be divided into three categories :—

1. Permanent. 2. Semi-permanent. 3. Non-permanent.

Owing to the necessarily superficial nature of the delustring deposit, the glazing effect of ironing, and the thermoplastic nature of cellulose

acetate to which hot embossing restores much of the original lustre, true permanence upon cellulosic materials cannot be ascribed to many delustring effects for which that quality is claimed.

1. Permanent Delustring Effects.

A permanent delustring effect will withstand, without appreciable increase in lustre, treatments of ten minutes' duration with 1 per cent. sodium oleate in a rotary washing machine (at 100° for cellulosic fibres, 80° for silk and cellulose acetate, 60° for wool), with intermediate rinsing and drying by means of an iron heated to 200°.

This class of effect is produced by the application of solutions of cellulose, its esters or ethers, usually but not necessarily in conjunction with a pigment; in order to enhance the effect, and to improve the bonding with the fibre, the latter may be subjected to the action of a solvent or swelling agent which increases the transparency of untreated areas.

Cellulose acetate or nitrate is usually employed, dispersed in organic solvents, or in calcium thiocyanate; the dispersing layer may be produced by deposition of the ester in a spongy form, but titanium white is usually present, while calcium may be found as oxalate, sulphate, or carbonate.

So far as the writers are aware, no other cellulose derivatives have yet found commercial application, but the extension of the method to dispersions of cellulose seems on economic grounds a reasonable expectation.

Faults.—(a) *Dusting.* This very objectionable defect is liable to occur whenever pigments are present in a finish, and appears to arise partly from the use of too small a proportion of the binding agent, and partly from the use of pigments which are not wetted, or are incompletely wetted by the dispersion medium. In view of the interest and importance which attaches to this defect, especially since the introduction of regenerated cellulose staple fibre, in itself an inexhaustible source of dust, a method of testing is given on p. 910.

(b) *Presence of Residual Solvent.* Solvents for cellulose esters and ethers frequently resist complete removal and give rise to odours during storage. Heating over water in a closed tube suffices to detect residual solvent, of which no trace is permissible.

(c) *Development of Free Nitric Acid.* This arises from instability of the ester, especially when the specific surface is large, as in the present case. When residual solvent is present, this defect is especially likely to ensue on exposure to light (see Stiffness, p. 864).

2. Semi-permanent Delustring Effects

A semi-permanent delustring finish is not commercially acceptable after the test described for permanent finishes of this type, but is little affected by treatment for ten minutes with 1 per cent. sodium oleate at 60° in a rotary washing machine, with subsequent rinsing and drying.

This group comprises several finishes including cellulose acetate delustred by soaping at the boil, steaming with urea, deposition of methylolurea resins, or treatment with mixtures of nitric and sulphuric acids, all fibres delustred by deposition of methylolurea, barium tungstate, and occasionally other barium or calcium salts, zinc or titanium oxides, β-stannic acid, silicic acid and silicates formed by double decomposition.

Faults.—(a) *Impaired Physical Properties of the Fabric.* The finishes above enumerated reduce the tensile and ripping strengths, and the resistance to wear to a varying extent. The deterioration may be very serious, especially in the case of cellulose acetate and regenerated cellulose fibres, which are sometimes scarcely coherent.

(b) *Development of Objectionable Odours.* This is met with, less frequently than a few years ago, in cellulose acetate fabrics which have been delustred in the presence of solvents, especially phenol and cyclohexanol. Subsequent treatment in hypochlorites accentuates the " hospital smell."

As a rule the odour is quite pronounced, and no test is necessary.

(c) *Local Variation in the Finish.* This defect is peculiarly prone to occur in the finishes of this group, since the cellulose acetate is readily relustred by pressure and heat, whilst a very small variation in one of several factors may cause barium tungstate or methylolurea resin to be deposited in the bath instead of the surface of the fibre, and the size of the particles is much more sensitive to conditions. The most common variation which gives rise to much loss is a gradual variation in the deposit from the selvedges to the middle, which often escapes detection until the fabric has been sewn into garments.

A lighting arrangement which produces even illumination across the inspection table is necessary, and the usual allowance of 20 ft. candles is quite inadequate owing to the small proportional differences which must be detected.

(d) *Permanent Distortion of the Fabric.* This is of common occurrence in delustred cellulose acetate fabrics, since the plasticity of the fibre gives permanence to any creases or folds which may be present. These cannot be removed from finishes of this type, since hot pressing would impair the finish, and the faults constitute irremediable damages.

3. Non-permanent Delustring Effects

A non-permanent delustred finish is injuriously affected by treatment for ten minutes at 60° with 1 per cent. sodium oleate in a rotary washing machine with subsequent rinsing and drying.

In addition to the difference in permanence these finishes usually differ in degree from the previous groups, since the object is to mitigate the orderly reflection of light from the fibre surfaces, and not to produce a full contrast between treated and untreated goods. Thus the finish finds most extended application in the sophistication of inferior goods, and two bath processes are excluded by considerations of cost.

Inorganic pigments, bentonite, titanium white, and china clay are usually employed, dispersed in the presence of a protective agent, but cationic fats, soaps of alkaline earth metal and aluminium are effective and may be met with in practice. The time of wetting of the fabric is much reduced by these substances.

I. WETTING

Ease of wetting by water is usually implied, but ease of wetting by varnishes, linseed oil, and other organic liquids is frequently required, which is, of course, a somewhat different matter.

No matter what liquid is used, it is necessary to reproduce so far as possible the conditions in which the fabric is to be used, since the time allowed for diffusion has important influence upon the quantity of liquid taken up.

Before any tests of wetting and absorbency are carried out, care must be taken to ensure that the properties of the fabric are stable to storage, since discontinuous fat deposits tend to form films with the passage of time. Moreover, in order to disguise an unsatisfactory preparation, wetting agents are occasionally added to the fabric, some of which are not indefinitely stable, while others migrate during storage, especially at higher temperatures, and form a water-repellent layer upon the fibre surface (see Storage, p. 911).

Faults.—The most common cause of poor wetting by water is the presence of lime soap deposits, from which few textiles are completely free.

Boiling in 1 per cent. sodium hexametaphosphate (Calgon) dissolves the deposit, and the sodium soap formed causes the solution to foam, the wetting time being much reduced.

Fatty residues less frequently give rise to trouble, but may be present in most textiles from time to time, and usually arise from the fats used in warp-sizing.

Such residues may be insoluble in organic solvents, and fluorescence

in ultra-violet light (p. 817), staining tests with osmic acid, or with fat-soluble dyestuffs, provide indications of the nature of the deposit.

Deposits which are aged and resist extraction by organic solvents may usually be removed by boiling for thirty minutes in 10 per cent. Emulphor EL, after which the fibre shows a diminished wetting time.

Deposits which resist wetting by fatty bodies are objectionable in goods which are to be finished in oil-proofed or varnished finishes. Such deposits are usually formed by drying upon the fibre a complex of degraded cellulose and amino-acids precipitated by iron hydroxide. Immersion in acidified thiocyanate solution usually gives a strong positive result. (See also Testing, below.)

The presence of starch residues is frequently responsible for local differences in the behaviour of a fabric to wetting, and is quite as objectionable as the presence of fat alone, since the less pronounced variation between the body of the cloth and the defective areas often escapes observation until serious amounts of faulty material have been processed. Moreover, the presence of residual starch is a clear indication of defective desizing, and is likely to be accompanied by local overbleaching. Finished cloths which are required to exhibit good and uniform absorbency should therefore be tested for starch as a routine precaution.

Fabrics required to exhibit quick and uniform wetting by liquids comprise cleaning and drying cloths of all types, and cloths for subsequent wet processing, proofing and coating, for which freedom from dusting is usually desirable, and frequently essential (polishing cloths, eye-glass cloths, typewriter ribbons). Cloths destined for such uses should therefore be examined as described in the section on dusting. (See also Transmission of Light, Obstruction of Interstices, p. 882).

Testing.—Tests for the superficial wetting of finishes are described in the section dealing with tracing clothes. (See Transmission of Light, p. 881.)

The most generally useful test depends upon the time of spreading of a standard fluid, conveniently, fountain-pen ink, until a meniscus is not visible. The conditioned fabric is stretched horizontally between two paper clips, and a drop of ink allowed to fall upon the surface from a burette fitted with constant level supply and stoppered at the top. The jet of the burette is inserted in a rubber stopper when not in use, in order to prevent formation of a deposit, and a few drops are run away prior to each test. A well-scoured smooth fabric of cellulosic fibres should show no meniscus after five seconds, and chlorinated wool should wet in five to ten seconds.

Silk, unchlorinated wool, and cellulose acetate are not used where great absorbency is required, and show a longer time before absorption

is complete. Traces of lime soaps and residual fat increase the time of wetting to eighteen seconds and upwards, hence the test is a sensitive method of following a scour or series of preparatory processes ; on the other hand, instantaneous absorption should occur on towellings, dish-cloths and dusters.

Eye-glass cloths, and special dusters which are required to leave a glass surface free from grease marks, usually contain a polyethylene glycol fatty ester or similar body, which will take up both fat and water. The efficiency is difficult to estimate precisely, but the following method gives a reasonable indication. A strip of plate glass 8×4 in. is cleaned with caustic soda solution, dried, and half immersed in 0·1 per cent. solution of lanoline in petroleum ether, dried, dipped in water and drained. The number of rubs required to produce even wetting of a strip the whole length of the plate, using a fresh place on the test fabric for each rub, varies according to the suitability of the fabric and of the finish.

Uniformity of wetting cannot usually be estimated directly, except from the variation between test specimens. It is, however, possible to obtain a fair indication of the presence of local deposits by examination of the whole of the fabric by ultra-violet light, and this procedure is recommended when such deposits must be detected (p. 817).

Wetting by organic solutions or liquids may be determined by the drop method, preferably using a fat soluble dyestuff to increase the ease of observation. Deposits which resist wetting by organic liquids commonly arise from the bleaching process, after scouring, and appear dark by ultra-violet light, whilst fatty deposits usually fluoresce.

J. Absorbency

This is a composite quality involving wetting of the fibre substance, spreading of the initial film along regular and unobstructed capillary channels, and storage of the absorbed water to the maximum extent in yarns which occupy the greatest apparent volume.

Owing chiefly to economic considerations absorbent cloths are rarely so finished as to produce the most satisfactory results, since the restricted circulation of water possible through such fabrics makes the efficient purification of the goods a difficult and costly operation.

Faults.—Incomplete size removal is a common fault in finishes of this type, and starch is frequently present in large quantities, while the fat content is rarely reduced to a figure (about 0·03 per cent.) which gives security against deterioration in wettability during storage.

A consequence of unsatisfactory purification is the lavish use of bleaching agents, to which is due the low viscosity commonly found in towellings, etc., resulting in reduced tensile strength and resistance to wear.

Deposits of lime soap are commonly present, and may be detected by boiling in sodium hexametaphosphate (Calgon), which dissolves them.

Reduced absorbency is caused by diminished thickness of the fabric ; this dimension should be tested as a routine operation in the examination of absorbent fabrics, towels, handkerchiefs and the like.

Dusting is frequently excessive, due to chemical degradation and to mechanical disturbance of fibres. (See Dusting, p. 910.)

Testing.—*Absorbency.* This may be defined as the ratio of liquid to dry material found when the fabric is impregnated in standard conditions. Many methods of determination have been proposed, differing essentially in the time allowed for absorption, and the force against which the fabric must retain the absorbed liquid. The conditions in which towels, dish-cloths, and similar articles are used necessitate the quick and complete absorption of a moisture film, while technical processes of impregnation may not permit the gradual replacement of the air in uneven capillaries by water. The writer therefore considers that the yarn should be spun, and the cloth so constructed as to provide for the smooth progress of water or other absorbed liquid into the capillary channels, with unobstructed exit of the air, and that fabrics which require prolonged immersion before the capillaries are filled do not satisfy the requirements of users.

The most satisfactory means of removing the surplus liquid is probably by suction, but, unless the fabric is uneven in thickness from place to place, the pressure between two rollers is quite satisfactory, and the apparatus is cheaper and less complicated. Centrifuging is not satisfactory unless a single layer of fabric is disposed without creases about the circumference of the basket, a laborious process, since the rim of the basket, which is necessary for mechanical strength, makes access difficult.

The apparatus preferred consists of a small squeezing mangle with narrow diameter, rubber-covered rollers, and a small trough about 10 cm. deep, in which is fixed a glass rod 1 cm. from the bottom.

A standard fabric, such as piqué or hair cord which combines regularity of weave with compressibility, and of known absorbency, is sewn to one end of the test specimen as a control. Both are passed through the trough, filled with the desired liquid, allowing one second to elapse between entry into the liquid and passage between the rollers.

Portions of each fabric are immediately cut and placed in tared, stoppered flasks, and the ratio of liquid to fabric determined for each case.

Allowance must be made for the hygroscopic moisture present before impregnation, but if the fabric is to be used with liquids which

do not dissolve water appreciably, the samples should preferably be dried prior to impregnation.

Rapidity of Spreading. This property is important, as the rapidity with which wet places lose the excess water does not depend upon the absorbency, and is in itself a desirable property. A sample 20 cm. square is fixed horizontally upon a frame, 5 ml. of standard ink or other liquid is delivered from a burette upon the middle point, as fast as possible, without allowing a drop to form upon the underside of the fabric, and the time which elapses between the opening of the burette and the disappearance of the meniscus at the central point noted. Residual sizing materials, or unsuitable balance of the cloth, are frequently made apparent in this test by the much greater rapidity of spreading along one system of yarns.

K. Resistance to Wetting

Like other finishes the shower-proof finishes which are becoming increasingly popular for general use may be divided into permanent, semi-permanent, and non-permanent categories, although at present true permanence has not been attained.

The method of finishing depends upon the production of a fatty film upon the surface of the fibre which is not wetted by water, and the resistance of the film to disruption by the use of alkalis and detergents determines the permanence.

The most usual type of shower-proofing consists in applying a wax emulsion and drying, while the permanence may be increased by a high temperature treatment. The fat film formed is not strongly adsorbed on the fibre and breaks up when treated with hot detergents.

More permanent results are produced by deposition of fatty acid salts, usually aluminium stearate, either from emulsions of a solution in organic solvents, or by double decomposition, by successive impregnation with alkali soaps and aluminium salts. If the deposition is followed by a heat treatment, these soaps give quite useful results.

The most permanent results involve either direct condensation with cellulose of an aliphatic acid, acid chloride, anhydride, carbonate, or isothiocyanate, linkage of a fatty acid derivative with cellulose by means of formaldehyde or glyoxal, or condensation upon the cellulose of a urea-formaldehyde or similar non-fatty resin in presence of an aliphatic residue possessing a water-soluble group at one end.

Direct condensed finishes are unlikely to be met with in practice owing to the expense of carrying out bulk reactions in organic solvents, while reactions involving direct union of reactive groups with cellulose at high temperatures are not yet commercially reliable.

A similar process which gives results resistant to dry cleaning has been used commercially to a limited extent during recent years.

This is similar to the aluminium soap method, except that a dibasic acid with a long chain alkyl substituent is used instead of a monobasic acid. From the latter finish it can be distinguished by insolubility in dry-cleaning solvents, and is differentiated from the stearamide-formaldehyde finishes by the presence of aluminium and resistance to treatment with mineral acid, followed by treatment in soap solution. The resistance of the finish to soap solutions is inferior to that of formaldehyde condensation finishes. Alignment of the fatty chains proceeds slowly, consequently samples of this finish should be kept for a week prior to testing for resistance to wetting.

Condensation with aldehydes is subject to limitation in the number of reactive groups possessing independent thermal agitation at the fibre surface, and to the reduction in tensile strength which occurs when fibres of orientated cellulose micelles are methylenated, while condensation by means of formaldehyde-resins is less dependent upon the chemical nature or activity of the fibre. The most widely used process, which depends essentially on condensation of formaldehyde with the fibre and with an aliphatic amide is similar in principle to the processes of condensing methylolurea on the fibre and is liable to the same defects. In particular, the resistance to washing with soap varies according to the mean temperature during condensation, and samples for testing should be taken from different places in several pieces, attention being paid to the possibility of variations from the middle of the piece to the selvedges. When condensation has not been efficient and the goods have not been washed after condensation a trace of pyridine may be present giving the goods a slightly unpleasant odour.

Faults.—The permanent non-wetting finishes are subject to variations in conditions of condensation in the same way as other high temperature condensations upon textiles. (See Creasing, p. 873). Variations in the fastness-to-washing of the effect, due to such causes, are more injurious in non-wetting finishes than in crease-resisting finishes, since the contrast between treated and untreated places is greater in degree and more readily detected. Several samples should therefore be tested for resistance to wetting after repeated washing in a boiling solution containing 1 per cent. sodium oleate and 0·5 per cent. sodium carbonate for cellulose fibres, and in 1 per cent. sodium oleate at 80° and 60° for wool and silk respectively.

Tendering of the cellulosic fibres is liable to occur in some processes owing to the inadequate buffering of the evolved halogen hydracids, and the tensile strength should be controlled as a routine test.

Semi-permanent and non-permanent finishes differ little from simple impregnations. Liability to rancidity should be examined by storage in a stoppered flask at 70° for a few days, or the iodine value of the extracted fats determined.

Shower-proofing processes which depend upon condensation of the fatty matter on the fibre, together with a second substance which diffuses more readily, such as monomethylolurea, are subject to surface concentration of the more mobile constituent during drying, unless the rate of evaporation exceeds the rate of diffusion, and the surface becomes case-hardened to some extent as described under Creasing, p. 873, while the fatty matter in the interior may be less fast to washing. To correct capillary separation the time of drying may be increased, especially after washing, but the case-hardening effect is unimportant unless excessive resin is present, and the fabric has been dried after impregnation in contact with a heated surface.

Testing.—*Resistance to Organic Solvents.* Permanent finishes must be permanent to dry cleaning. The fabric may be extracted with a suitable solvent, trichlorethylene, for example, and subsequently tested for resistance to wetting.

Fastness to Washing. The test pieces are boiled in a solution containing 1 per cent. sodium oleate and 0·5 sodium carbonate for half an hour, and tested after conditioning for resistance to wetting.

Resistance to Wetting. The fabric is spread horizontally, and tested with ink as described under Wetting (p. 892). Resistance should be complete, and the deposit from an Alkali Blue ink should, after drying, be removed completely when rinsed in cold water.

Efficiency of Treatment. Sufficient mechanical force will cause water to enter the interstices of a fabric of unwetted fibres, whilst, on the other hand, perfection of the non-wetting film throughout the fabric is comparatively rare. Absorption of water decreases the vapour tension, and the rate of drying in a desiccator shielded from light and heat in a thermostat is characteristic for each fabric of the amount of absorbed water present, since interstitial water will have normal vapour tension, or slightly more than normal if present in very minute globules. The fabric is wetted out in 0·25 per cent. Nekal B Ex. at 60° until saturated, subsequently rinsed in water, squeezed in the small mangle described under Wetting (p. 894), and desiccated flat on a watch-glass upon the pan of a balance fitted for external operation, the case constituting the desiccator. The drying process is followed at intervals of ten to thirty minutes according to the weight of the fabric. This test may conveniently be carried out upon the soap-tested sample.

Sewing Strength. A reduced coefficient of friction is necessarily reflected in a certain reduction in sewing strength which may be accentuated by excessive tension, and should therefore be controlled in utility fabrics.

Permeability. This is a measure of the force required to drive a fluid, usually water but sometimes oils or varnishes, through the

interstices of the fabric; the capillary spaces of the yarns are comparatively unimportant if the cloth has been proofed.

The property depends chiefly on the construction of the fabric, but is much influenced by finishing operations, such as beetling and chasing, which increase the compactness of the structure and the regularity of the yarns. Owing to irregularities which arise in spinning and weaving scattered results must be expected, and unless the finish is intended to be impermeable there is little object in performing the test. The usual methods of testing involve direct measurement of the water column which will drive the surface film through the fabric.

A simple and convenient apparatus may be constructed from a flanged steam-pipe of 2 in. internal diameter and 10 or 12 in. long. The pipe is held vertically, and to the upper end is secured a plate fitted with a brass thistle funnel of 100 ml. capacity and an ordinary Schrader valve, while the specimen, tensioned on a spring ring, rather larger in diameter than the flange, is clamped to the lower end between rubber-covered fabric washers.

When the specimen is in place, the water, oil, or other fluid is run in and the pressure raised to the desired figure by an ordinary tyre inflator attached to the valve, or increased until the fluid appears on the under side of the fabric.

Some fabrics, such as awnings, tent cloths, etc., which are required in service to absorb only small amounts of capillary moisture, should be tested for some days under small pressures, in addition to the quicker test at a higher pressure.

The test gives useful information only with evenly and closely woven fabrics, and is not applicable to ordinary dress goods which are usually of irregular texture.

L. Fixation of Dyestuffs

Fixation may be regarded as the means whereby a dyed fabric may have its fastness to light, washing or friction increased. Fixation might perhaps be regarded as a means of so altering the dyestuff, the method of dyeing or the method of finishing, as to promote resistance to other conditions such as mercerizing, soda boiling, marking-off, spotting, proofing, etc., but it is commonly applied only to improvement of the dye as regards resistance to light, washing or rubbing.

In deciding upon the means to be employed in the fixation of any dye, it is essential to know the particular characteristics of the dyestuff.

Innumerable patents claim methods of fixation to light and washing. The fastness of direct dyes to light, and in many cases to washing also, is often, but not always, improved by treatment after dyeing with

copper sulphate, with or without potassium dichromate, or with chrome alum. These salts are used in presence of acetic acid. The fastness to washing of direct dyes is sometimes improved by after-treatment with formaldehyde in presence of acetic acid.

Before attempting to improve the fixation of particular dyeings, it is always wise to be assured that the method of dyeing employed has been satisfactory, for improperly dyed fabrics may not be improved by after-treatment with the above-named substances.

The fixation of Naphthol or Azoic dyes, so as to make them fast to rubbing, is commonly attained by thorough soaping together with as much mechanical movement as may be practicable ; but since this treatment has little more effect than to remove more or less " surface colour," *i.e.* the particles of dyestuff which are not embedded in the fibre, its necessity should be avoided, if possible, at an earlier stage. It is not always possible to avoid some superficial precipitation of the naphthol complex and the dyer has to exercise all his art, as well as his science, to reduce the amount of surface colour to the minimum.

In a general way it may be said that fastness to light or washing increases with the degree of aggregation of the dye as it exists in the fibre, and that treatment with copper, chromium or formaldehyde improves the flocculation of the dyestuff.

M. SHRINKING

All fabrics as they come from the loom are in a more or less strained or stretched condition owing to the mechanical conditions of spinning and weaving.

Fabrics are frequently treated chemically, mechanically, or by combined processes in order to reduce the shrinkage which occurs in washing.

The methods employed may be classified as follows :—

1. *Pre-shrinking.* This method aims at producing a finish which has been subjected to the operations causing shrinkage in wear, in one or more cycles. Usually the method comprises washing in hot soap without tension, drying in a relaxed condition, and, if necessary, repetition until the shrinkage is satisfactory.

2. *Mechanical Shrinkage.* Contraction of the warp is generally attained by some mechanical device which receives the fabric at a certain speed and delivers it at a slightly lower speed, while preventing, however, such puckering of the fabric as might be expected under those conditions.

This mechanical or " compelled " shrinkage of fabrics involves the keeping of careful control over the degree of shrinkage to which any single piece or number of pieces is or are subjected. It is usual

to apply a "shrinkage test" to samples of cotton fabric taken from the material which is to be submitted to the process, these samples having parallel lines marked upon them in both directions either 12 or 20 in. apart. The samples are treated as nearly as possible as they would be in ordinary laundering, except that care is taken at every stage to avoid submitting them to tension. After the ironing and drying, the average distance between the lines is taken and the machinery is so adjusted as to affect the same proportionate dimensions in the whole of the piece or pieces as was shown by the samples. When a guarantee is given with the goods, it is generally to the effect that they will not shrink in use more than, say, 1 per cent., or some such figure. This means in reality that they will fulfil the guarantee provided that the shrinkage test in question is regarded as the standard of complete shrinkage. Different authorities conduct their shrinkage test in slightly different ways, and a recognized standard method is much to be desired.

The warp tension on different looms varies greatly, indeed the tension on one loom may be found two or three times greater than upon another loom making similar fabric. Thus pieces of the same cloth from the same shed have shown 18 and 35 per cent. warp crimp respectively. Consequently it is not surprising that when the same degree of shrinkage is demanded in a large number of pieces, many of them may be found to show wide variation when submitted to a "shrinkage test" after the shrinkage process. It may become necessary to test every piece and to adjust the machine to suit each piece.

3. *Fixation of Set.* In this group are comprised processes which fix the set of the fibres more or less permanently, thus preventing changes in the structure of the fabric. The non-permanent methods usually employ a heat treatment after the fabric has assumed its desired dimensions in order to prevent shrinkage during storage (hot pressing, dekatizing).

More permanent fixation of set is produced by cementation of the fibres with binding agents which are rendered insoluble during heat treatment, or other method of fixation, such as protein methyl-cellulose hexamine mixtures; superficial solution of the fibres in non-aqueous solvents, usually sulphuric acid, permits the relaxation of strains and the resetting of the structural units of the fibre, while cementation may also be observed; wool is customarily chlorinated, partly in order to improve wetting by water, partly to reduce shrinkage; finally, the condensation of formaldehyde resins upon cellulosic fibres, commonly used to reduce elastic after-effect, stabilizes the set of the fibres during condensation when the operation is carried out at sufficiently high temperatures.

Different methods of reducing shrinkage are very often combined

to produce a more perfect result ; in particular methods (1) and (3) are frequently mechanically adjusted in the final process for the sake of accuracy.

Faults.—1. *Pre-shrinkage.* The only fault which can arise directly from pre-shrinking methods is due to a configuration in the fabric unstable to subsequent laundering and drying operations.

2. *Mechanical Shrinkage.* The most common defect shown by mechanically shrunk goods is the presence of excessive crimp in the warp, and occasionally insufficient crimp in the weft ; this results in corresponding dimensional changes both in wear and during the initial laundering, since the excess crimp is very loosely held due to excessive extension of the warp prior to the shrinking process. The most characteristic feature is shown by the warp load-extension curve which runs almost parallel with the extension axis at very low loads, for 2 to 5 per cent. extension.

3. *Fixation of Set. Non-permanent.* The non-permanent methods of fixation, which involve only heat treatment in steam, are among the simplest finishing processes, and are subject only to variation in the degree of treatment.

Permanent. Processes involving cementation of the fibres or solution of the surfaces necessarily increase the stiffness, and are discussed under that heading (p. 864).

Processes involving fixation of the fibre configuration by condensation with formaldehyde resins, which represent a subordinate aspect of crease resistance, are subject to the faults discussed under that heading (p. 873) and to the following :—

Unstable Dimensions. When the condensation of the resin is complete (not a common occurrence in practice) the form of the fibre is stabilized during cooling after condensation. When the dimensions of the fabric are changed in any direction by finishing operations carried out at a temperature below that of the condensation, contraction or relaxation to the original configuration and dimensions takes place during laundering, or even upon storage.

Superficial local deposition of resin in a discrete layer may be caused during mechanical shrinking of goods containing insufficiently condensed resin. The temperature employed in the (Sanforizing) shrinkage process may exceed that attained by the fabric during condensation ; the uncondensed resin becomes plastic, adheres to the hot surface of the shrinking cylinder, and may retransfer locally to the fabric. Surface glaze and stiffness arise from the same cause ; microscopical examination, and removal of the resin will indicate the nature and extent of the resin deposits.

Chlorination of wool carried out in aqueous solution is particularly liable to variation ; excessive chlorination causes embrittlement of the

fibre, increased ease of wetting and dyeing, and reduction in the extensibility, the ripping and tensile strengths. Despite the reduction in shrinkage due to felting, fabrics may be extended during subsequent processes, with consequent shrinkage when the temporary set is relaxed. This extension may be masked by mechanical shrinking (p. 899), whilst the reduced strength may be mitigated by finishing in lubricants. (See Creasing, p. 873.)

Condensation with formaldehyde resins does not appreciably reduce the shrinkage of woollen fabrics, and is rarely employed on this fibre.

Testing.—The load-extension hysteresis curves are the most characteristic and readily executed tests applicable to the detection of abnormalities in shrinkage and extensibility. (Suitable appliances are marketed by Louis Schopper and The Tensometer Co. See p. 700.)

Liability to Dimensional Changes. Samples, which may conveniently be 20 cm. each way, are cut from the neighbourhood of the selvedge, and from the middle of the piece : the cuts should be along the warp and weft, since in many cases the threads do not interesect at right angles, owing to faulty finishing.

The set of samples is treated for five minutes in a bath containing 0·5 per cent. sodium oleate with constant agitation at 60° in the case of wool and cellulose acetate, 100° for cellulosic fibres and silk, rinsed in soft water at 60°, supported upon wire gauze, dried by means of an air blast, and carefully ironed without tension. If the shrinkage or extension does not exceed the guaranteed figure (usually 1 per cent.) after three treatments the samples usually alter little in subsequent repetitions, but doubtful cases should be subjected to six treatments.

The angle at which warp and weft intersect is most important to the user of fabrics, since in washing the fabric relaxes until the yarns intersect at right angles, with consequent dimensional changes in made-up goods. The question has not been given attention proportional to its nuisance value, whilst much less important points have been the subject of prolonged investigations. Whilst the provision of standards for general textile merchandise must await the awakening of the industry to the importance of the matter, it seems of little use to guarantee that the length of threads shall within certain limits remain constant after washing, unless the same standards apply to any dimension of the fabric. The writers therefore suggest that the diagonals of a parallelogram formed by warp and weft should not increase or decrease after washing to an extent greater than the tolerance permitted to warp or weft separately.

Excessive Crimp. Samples cut as before are relaxed for five minutes in water at 60°, suspended from a pin passed through the corners during drying ironed and measured. Excessive crimp will usually be shown by extension of the warp.

N. WEIGHTING

The practice of weighting fabrics, apart from its persistence in the traditional and less advanced sections of the silk and cotton trades, has in recent years tended to diminish ; the proportion of merchandise loaded, and the quantity of the weighting materials in relation to fibre have alike been reduced, to comply with the increasing demand for fabrics capable of remaining unchanged in colour and in properties under conditions of use.

In accordance with the endeavours of technologists to increase the functional efficiency of commercial products the adulteration of cotton fabrics by filling with 200 per cent. of barium sulphate suspended in starch, and the swelling of silk to accommodate comparable amounts of iron tannate, or tin phosphate is increasingly confined to fabrics which are not washed, and in silks to the ephemeral types of fashion fabric.

The increase in weight which results from modern finishing operations is in most cases incidental to a process aimed at improving some other feature, such as the draping qualities, crease resistance, or wear, although the resultant weight increase frequently attains 25 per cent., and is comparable in itself with the gain due to moderate loading of the fibre or fabric.

Economic factors limit the range of substances used for simple weighting processes, but the same considerations do not seem to apply when the weight increase is incidental ; and large quantities of aliphatic alcohol sulphuric esters, in particular, may be found upon natural and artificial silks, and even upon knitted cotton goods.

The foreign substances which contribute appreciably to increase of weight without producing a marked stiffening are :—

1. Organic sulphonic acids and sulphuric esters and their salts, which are rarely employed in quantity on cotton or lower priced artificial silk materials.
2. Synthetic resins produced by condensation in the fibre, which are almost invariably methylolureas, and mixtures of this resin with organic compounds of high molecular weight containing at least one hydrophilic group.
3. Soluble salts of metals, or of ethanolamines, the last named being confined to the more expensive fabrics.
4. Boric acid, boric esters of glycols, odourless organic compounds containing hydroxy groups, glycols, glycerol, sorbitol, glucose, which, according to price levels, may occur in all grades of fabric.
5. Insoluble complexes and salts deposited in the fibre which are found on natural silk, and in smaller quantities on regenerated

cellulose fibres: the constituents include mixed hydroxides of antimony, silicon, tin (which may occur alone), tungsten (used to increase dispersion of radiation), phosphorus, aluminium, and barium, insoluble salts of barium, and chromium or iron tannates in black silk; hydroxides of chromium, iron, and manganese alone or in mixture.

6. Ferro- and ferri-cyanides of iron on window-blind fabrics, may be added to the list, although employed as dyestuffs.

Substances which contribute substantially to an increased weight together with an increase in stiffness, include resins deposited upon the fibre, esters and ethers of cellulose, starch, acetylated starch, degraded starches, and mixtures of the foregoing substances with each other, and with smaller quantities of albumin, gelatin, ammonium caseinate, or alginate, and hygroscopic compounds, plasticizers, and soluble or insoluble salts of inorganic bases.

Faults.—Certain defects which result from weighting operations are peculiar to weighting with particular classes of substance. Defects arising directly from stiffening operations, crease-resisting finishes, and other cases not specifically concerned with the weight of the finished fabric as such, are dealt with elsewhere.

Faulty Conditioning. Finishes dependent upon the presence of hygroscopic substances are rarely allowed to attain equilibrium with atmospheric conditions, and the exposed portions show to a pronounced degree, the defect of alteration in storage (p. 911). This applies especially to glycol boroborate esters.

Lack of Tensile Strength after Ironing. Finishes containing soluble salts may show a loss of tensile strength after ironing; this defect is permanent if acid is present, but temporary if due to crystallization; magnesium chloride is especially injurious.

Lack of Tensile Strength after Treatment in Alkali. A marked reduction in the tensile strength occurs when fabrics of regenerated cellulose, which have been treated in aluminium salts such as the acetate or formate, are subsequently heated at high temperatures with alkaline solutions; the wet strength may be reduced to a very low figure. If aluminium is present the loss of strength after boiling for thirty minutes in 1 per cent. NaOH should be determined.

Loss of Tensile Strength in Storage. This may be caused by neutral salts, insoluble inorganic compounds, acids, or substances which give rise to acids: fabrics of regenerated cellulose, natural silk, or cellulosic fibres which contain inorganic salts should be stored at a high temperature, and the deterioration observed. (See Storage, p. 911.)

Estimation of Weighting

This is not always possible, while in rare instances the question of defining the true weight is difficult; for example, cellulose which has been etherified with ethylene oxide, glycide, or chloracetic acid may be increased in weight very considerably, but the increase scarcely seems to be weighting in any customary sense. Similar instances are likely to multiply in the near future, as the technique of linking fats, dyestuffs, or finishing agents chemically to the fibre finds increased application, and it appears that short of complete hydrolysis of the aggregate, and determination of the products of hydrolysis arising from the fibre, estimation is not practicable, unless an untreated sample is available.

When the fibre has been united with a similar product, cellulose with cellulose, wool with albumen, gelatin or casein, it is probably as accurate to estimate the extent of the addition from the change in physical properties as to attempt selective removal of the added matter. Selective absorption methods are completely misleading, since such deposits stain with dyestuffs to a very variable extent, dependent on the conditions of precipitation and after-treatments.

At the present time, some manufacturers of cellulose derivatives and plastics add a small amount of a characteristic substance to these products. General and uniform use of this device would be a substantial aid to the textile chemist.

The methods of extraction given below provide a reasonable indication of the content of various types of finishing agent. It is necessary to mention that mixtures of all kinds are used in practice; when one constituent is attacked loss of other constituents occurs, although the operation would not affect such constituents if used alone or with others of the same type. Similarly, most soluble organic bodies may be so fixed by synthetic resins as to resist solution by agents which do not affect the resin.

Unstiffened Finishes. Extraction with cold water removes hygroscopic substances and soluble inorganic salts.

Extraction with a solution of 5 per cent. hydrochloric acid and 1 per cent. citric acid at 80° for thirty minutes removes urea-formaldehyde resins, iron, chromium, and aluminium, manganese, some tin, cationic fats, and to a small extent organic bodies (usually softening agents) containing a water-soluble group.

Extraction with cyclohexanone at 80° removes most organic compounds, resins, ethers and esters of cellulose, and strips dyestuffs to a large extent.

Extraction with cold 5 per cent. hydrofluoric acid removes silicic acid, which may be present on silk or regenerated cellulose.

The above extractions will not damage cotton, wool, silk,

regenerated celluloses, or linen, unless formaldehyde is present, in which case cellulosic fibres will condense to form a methylene ether. (See Creasing, p. 873.)

If the amount of the specimen permits, the ash should be examined, using an untreated sample for comparison.

Stiffened Finishes. These may be divided into two categories, according to whether the stiffness is or is not considerably diminished by wetting with water at 60°.

(*a*) The stiffness is considerably diminished by wetting with water. Extraction with a mixture of 5 per cent. hydrochloric acid and 1 per cent. citric acid at 80° for thirty minutes removes hygroscopic substances, soluble inorganic salts, most insoluble inorganic salts and hydrates, dextrin, and to a large extent locust bean mucilage, gums tragacanth, arabic, senegal, and talha, starch and some organic softeners. Extraction with diastatic ferment for two hours at 45° will remove starch.

Extraction of cellulosic fibres in 2 per cent. caustic soda, and 1 per cent. sodium oleate will remove most organic matter except high viscosity cellulose filling and water-soluble methyl cellulose, which are not removable. Degraded cellulose will also be removed.

Extraction of animal fibres in cyclohexanone will remove polyvinyl resins and most of the aliphatic and aromatic compounds likely to be present.

Extraction with 1 per cent. sodium oleate and 1 per cent. Na_2CO_3 at 60° for wool and 80° to 100° for silk will remove alginic acid, gelatin and casein-formaldehyde compounds, and any degraded portions of the fibre. Albumin condensed by heat with hexamethylene tetramine cannot be removed without injuring the fibre.

(*b*) The stiffness is resistant to water at 60°. Extraction with cyclohexanone at 80° will remove ethers and esters of cellulose, organic weighting and softening materials, and all natural and synthetic resins likely to be present, together with associated mineral matter.

Extraction in 5 per cent. hydrofluoric acid and 1 per cent. citric acid in the cold will remove most of the residual mineral matter.

O. Sewing Strength

Since textile fabrics are not generally used as single pieces, but as two or more pieces united by sewing, the effective strength of the sewn assembly cannot be greater than that of the sewing. Hence determination of the strength of a sewing joining two pieces of the fabric is one of the most necessary tests if a utility fabric is under examination.

The proximate causes of sewing failure are the weakness, either of

warp or of weft yarns, and the lack of resistance to displacement of one system of yarns in relation to the other.

Weakness of Yarns. Weakness of one system of yarns is almost universal in fabrics composed of regenerated cellulose rayon, or silk yarns, one way, and cotton yarns the other way, which have been dyed, printed or finished, since each movement of the fabric causes the cotton yarns to abrade the lighter system.

The degree of abrasion varies with slight variations in construction of the fabric, since abrasion takes place at the yarn surface : coarser yarns and coarser filaments are therefore much more resistant to this type of internal abrasion than fine filament yarns of low denier. The change to a finer filament or a slightly lower denier yarn in cloths of similar construction has frequently resulted in the tensile and sewing strengths of the finished fabric being reduced to figures not acceptable for commercial use. This type of weakness is not necessarily accompanied by chemical degradation, and if the sewing strength test is unusually low, while viscosity figures are normal, microscopical examination will usually show ruptured fibres or filaments corresponding with the points of intersection of warp and weft, the injured yarns being readily split up into fragments when dissected from the fabric and pulled.

Such cases offer difficulty in the allocation of responsibility for the damage, on which point the tester may be asked to give a decision. On the one hand, the fabric could not be finished without causing injury to the weaker yarn system, while conversely, such fabrics are generally manufactured to a low specification, and a very small reduction in strength may render the goods valueless as merchandise. The writer suggests that a reduction of 20 per cent. in the sewing strength of fabrics containing a weak yarn system is a reasonable allowance for finishing processes.

Slipping of Yarns. This defect, also, may be due to the construction of the cloth, or to finishing operations. The most usual constructional defect is the reduction in the number of picks below the safe minimum for the type of cloth, since the crimp of the warp is the chief factor which prevents displacement of the weft : it is, however, necessary to observe that the insertion of excess crimp by mechanical methods (see Shrinking, p. 899) is not effective in reducing the slip, except in so far as an increased number of weft threads may be left between the needles and the cutter, since immediately tension is applied the crimp reverts to the normal figure.

The question whether the lack of crimp, and consequent low resistance to slip, results from excessive warp tension during weaving or during finishing arises in practice. If the constructional particulars of the cloth are available, the weft count alteration may give some

indication, but it is not possible to rely upon the examination of short reference samples, since short samples from pieces woven under excessive tension shrink during storage and are not necessarily evidence of the number of picks per inch originally shown by the bulk. Estimation by weight of the warp/weft ratio gives a more reliable indication, since this quantity remains unaffected by finishing operations, while excessive tension upon the warp during weaving sensibly diminishes the ratio in comparison with the normally woven fabric.

An additional indication may be furnished by the selvedge threads, or effect threads, since these are extended equally with the warp threads during finishing operations.

If the selvedge or warp effect threads, when dissected from the fabric and relaxed in hot water, do not contract approximately to the same extent as the ordinary warp yarn, the weaving tension is probably responsible for the deficient crimp.

The methods adopted to improve the sewing strength of cloth fall under three headings :—

1. Increase in the warp crimp.
2. Increase in the coefficient of friction of the yarns.
3. Cementation of the yarns by means of sizes.

1. When the warp crimp is increased by pre-shrinking methods (see Shrinkage, p. 899) the sewing strength is considerably and permanently increased ; the insertion of excess crimp by mechanical means is not so effective, and gives rise to the undesirable possibility of permanent local extension occurring during use.

2. This is usually effected by impregnating the fabric with ammonium resinate, an emulsified solution of high melting coumarone resin in an organic solvent, or by forming a deposit of urea-formaldehyde resin upon the fabric, the first being removed by washing, the second and third methods giving more permanent results.

All these processes are subject to certain drawbacks, in addition to the possibility of process faults as described under Stiffness and Creasing (pp. 864 and 873).

The increased coefficient of friction reduces the wear and ripping strengths, sometimes very seriously if cementation takes place, while the sewing properties of the fabric may be injured : the writer has examined fabrics which were for practical purposes unmachinable to the maker-up owing to brittleness and a high coefficient of friction, which gave rise to needle breakage. Also, the lustre may be reduced, especially by the urea-formaldehyde resin, an effect which is particularly evident when the treated fabric is dyed a deep shade.

Fabrics which have been treated in order to increase the sewing

strength must therefore be examined with care for deterioration of other properties.

Testing.—The method usually employed for testing the sewing strength of a fabric is to join two strips of the fabric by a sewing and measure either the breaking load or the load which displaces the sewing by a certain distance. Owing to the action of the expanders commonly employed in finishing works, and especially certain types of mercerizing machine, the middle of the piece is usually stretched and contains fewer ends per inch than the district 3 to 4 ins. from the selvedge: strips should therefore be sampled from various positions across the piece.

Comparative tests upon the same construction of cloth can always be carried out by this method, but the setting of standards of sewing strength for cloths of various types is not easy.

In addition to the structure and moisture content of the fabric itself, the type of stitch, the number of stitches per inch, the type and count of the sewing thread, and the tension of the fabric and of the thread during sewing all cause considerable variation in the test results.

Before this, as before all physical tests, the fabric to be tested should be allowed to condition together with the standard of comparison.

Those types of stitch which involve any binding action, or bending of either thread system are very sensitive to variations in tension and straightness of the sewing. The blanket type of stitch which makes a butt joint, the binding thread running at right angles to the sewing (Merrow Machine) gives more reliable results for the purposes of testing.

The margin tested (the space between the sewing and the cutter) is very important, since if a wide margin is used considerable slip may take place, until the packing of the displaced threads offers greater resistance; if margins of $\frac{1}{8}$ and $\frac{1}{2}$ in. are tested this objection is overcome.

The count of the sewing thread and the number of stitches per inch require variation according to the yarn count and pick of the fabric under test, in order to maintain a reasonable relationship between the two components. One stitch to each four or five ends is satisfactory, the sewing thread (of natural filament silk) being 60 per cent. heavier than the corresponding yarns of the test piece.

Difficulties may be experienced from the presence of filling material, and if the fabric under test is likely to be used in a washed condition, a more useful determination will be obtained by removing the size by malting, followed by boiling in water (to remove locust bean mucilage) in sodium oleate and sodium carbonate solution, and finally rinsing in hot water.

Unsoftened mineral khaki is difficult to sew satisfactorily. The

needle gets very hot, and even with a long stitch many threads are broken right through and others much weakened by cutting. If very short stitches are used on *any* fabric the yarns suffer badly.

Fraying. This is closely allied to slipping, but in some cases is fundamentally distinct. Some fabrics which fray very badly slip but little, or only slip at the seams after laundering, and when the margin beyond the seam is too restricted. A fabric which frays badly may need a margin of more than half an inch if slipping of the seam is to be avoided. The test is a simple one. A portion of cloth, 4 or 5 in. square, is cut from the piece, the edges being parallel to the warp and weft. This is cut by a diagonal into two test pieces. Similar test pieces should be prepared from fabrics already known to be, or suspected of being, of good and of bad resistance to fraying. All the test pieces are submitted to a "standardized" laundering process in which the amount of mechanical movement or rubbing of the cloth is pronounced. After drying and ironing it is easy to observe any difference between the amount of fraying produced in the several samples. If a quantitative test is desired, the sample may be weighed before and after cutting off the frayed edges (the three edges separately if desired), the result being stated as the percentage of fraying. In many fabrics the fraying is confined to within an eighth of an inch of the cut edge, but in some it will be found to exceed half an inch, and in such cases complaints will arise of "splitting at the seams" after washing.

Spun rayon fabrics are liable to fraying, and it may be found impracticable to avoid the defect and yet to maintain the desired and attractive construction and softness of the goods.

P. Emission of Dust

This defect, which is common to most finishes containing pigments and to fabrics of staple fibre, although objectionable, particularly to packers and making-up factories, is seldom given attention until the nuisance becomes intolerable. Apart from the hygienic aspect, the emission of pigment dust is indicative of faulty balance between the pigments and binding agents, whilst fibre dust usually arises from mechanical damage resulting in effect in reduced staple length.

A reasonable indication of the behaviour of fabrics in this respect can be obtained from the simple test here described, based upon the sharp reversal of curvature by which dusting is caused in practice.

The apparatus (Figs. 145 and 146) consists of two blocks built up from mild steel sheet about 16 gauge, each block consisting of six wide pieces 4×6 cm., spaced apart by three long strips 8×2 cm. between each pair, thus giving the effect of a comb. The six projecting

edges of each block, ground to a rounded form and polished to avoid plucking of the test pieces, are arranged vertically with about 2 mm. overlap in a stout wooden case.

This box is recessed at the bottom to receive the projections of the long strips, the blocks of sheet-iron strips being inserted through a panel cut in the (fixed) lid. The panel is recessed to correspond with the projections in a similar way to the bottom, but is cut down in width to 7·8 cm. to permit the insertion of the distance piece, which is pushed in to hold the assembly in position ; the ends of the box are

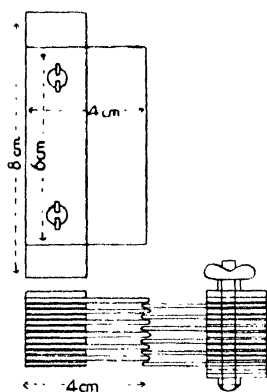



Fig. 145.

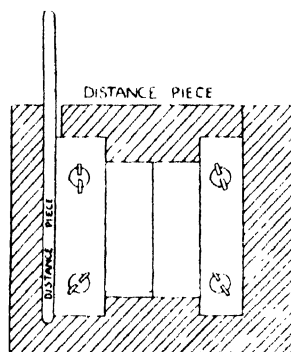



Fig. 146.

cut away to allow the passage of the test strips and the insertion of the glass dish which receives the dust.

In operation the side distance piece is withdrawn, followed by the top distance piece, and the left-hand block pushed aside to permit the threading of the apparatus, after which the pieces are again placed in position.

The test pieces cut with the guillotine 2 in. wide and as long as possible are sewn at each end to strips of fabric coated with nitrocellulose, which serve to precede and follow the test pieces and do not form dust. The actual test is performed by drawing the test strip once through the box, avoiding creases, and examining the deposit in the dish.

If a sufficient number of test pieces is run through, the deposit may be estimated, but exclusion of dust would be necessary, which involves more precautions and time than the figures are worth, since the extent of the deposit is visibly greater when defective goods are tested.

Q. Storage

Lack of permanence during storage is one of the most objectionable defects which textile materials can exhibit. The natural fibres, animal

and vegetable, are little subject to alteration, but the introduction of quick bleaching methods, insoluble azo dyestuffs, oxidation dyestuffs, vat dyestuffs and indigosols, and unstable organic bodies as finishing agents of all types, and the lack of sufficient after-treatment to ensure that impurities are removed, and the dyestuffs in the most stable state of aggregation all increase the sources from which defects may arise during storage.

Examination for defects liable to arise in finished goods is usually based upon intimate knowledge of the processes involved in the production of each particular shade and finish, the residues which may be present, the probable changes in state of aggregation, and the possible defects which may arise at each stage; commercial exigencies do not usually allow those concerned in the production of textiles to devote sufficient time to the problem, and methods of testing for some defects are completely lacking.

The writers here endeavour to review the principal sources of storage defects, and tentatively suggest methods of testing which may prove of some service pending more detailed examination of the question. Defects arising from finishing are dealt with under the appropriate section.

Sources of Odour

Amines. Insoluble azo colours, aniline black, diphenyl black, paramine and allied browns; occasionally direct dyeings which have been treated with azoic active components.

Phenols and Naphthols. Insoluble azo colours, delustred cellulose acetate.

Formaldehyde. Urea-formaldehyde resins, use of formaldehyde with neutral salts when applying cellulose derivatives.

Alkylamines. Softening agents containing alkylamino residues. Urea-formaldehyde resins containing methyleneureas.

Higher Aldehydes. Oxidation of unsaturated alkyl chains from residual soaps or softening agents.

Change in Shade of Dyestuff

General Causes. Insufficient conditioning of the material prior to packing frequently gives rise to change in state of aggregation of the dyestuff as the moisture regain becomes normal. Goods of all fibres which have been exposed to high temperatures, especially in the presence of formaldehyde, show this defect in a high degree, since conditioning proceeds very slowly.

The presence of alkali in finished goods gives rise to changes in state of aggregation, as the fabric becomes neutral through taking up CO_2 and SO_2 from the atmosphere. Vat, indigosol, and sulphur

dyestuffs may exhibit a change in shade, apart from physical causes, if the dyeing has been inadequately soaped. Dyestuffs sensitive to acid are still met with, and should be suspected if profound change in shade occurs (see p. 767).

Insufficient after-treatment is a fundamental cause of undue lack of fastness to light, change in shade and fading on storage, tendering of the fibre on exposure to light, and bleeding during washing.

Insoluble azo, vat, indigosol, and sulphur dyestuffs, which are rendered insoluble by chemical change in the molecule, do not immediately separate after precipitation from the water with which they are associated, but usually form a hydrated amorphous adsorpate which may assume the massive dehydrated, usually crystalline form only after prolonged boiling. The thermal energy and accessibility of the dispersed form give rise to inferior fastness properties, and when acted upon by heat, light, and moisture assume the more stable configuration with consequent change in shade. In addition to these physical defects, some vat, indigosol, and sulphur dyestuffs are prone to the formation of aggregates which, during oxidation and hydrolysis, become covered by an inert film, which restricts further development, while in dyeings upon wool or cellulose acetate the dyestuff may penetrate between the protein layers, or become dissolved in the cellulose acetate, which sometimes restricts the access of the developing bath to a still greater degree.

If these partly oxidized dyeings are treated by permanent finishing processes remarkable colour changes may ensue on storage or exposure to light; the only satisfactory test of these dyeings is exposure to sunlight of sufficient samples, since the photochemical reaction cannot be simulated by chemical methods. Usually the reaction proceeds very rapidly, and eight hours' exposure to sunlight will suffice to indicate the possibility of change. While accelerated fading tests with the carbon arc show some general relation to sunlight tests, the writer has not found either positive or negative results to be reliable.

Change in Shade of the Undyed Fibre

This may arise from many causes, of which the principal are oxidation of the degraded fibre, oxidation of oils or fatty softening agents, especially mineral oils, which are frequently added to printing pastes and left in the fibre after washing, re-oxidation of colouring matters which have been decolorized by reduction methods but not removed, and the oxidation of amines and naphthols which may be locally or uniformly distributed throughout the goods, or may be absorbed from adjacent materials. Growth of micro-organisms gives rise to a considerable number of colorations, which, however, are readily distinguished by microscopical examination.

Fading of Dyestuffs

Many direct, basic and acid dyestuffs fade rapidly in diffused daylight: unless special requirements necessitate the use of such fugitive colours, such fading is not commercially acceptable.

Loss of Tensile Strength

This is usually the result of acid hydrolysis: the acid may be residual, or may be produced upon the fibre usually by oxidation of compounds or dyestuffs containing sulphur.

Inorganic weighting of silk also produces tendering, especially in slightly acid conditions; the presence of neutral salts promotes the hydrolysis of this fibre, whilst the growth of micro-organisms may cause loss in tensile strength of all fibres except, in normal conditions, cellulose acetate.

Shrinkage

Fabrics are frequently woven too narrow to allow sufficient margin for shrinkage during finishing; such goods are commonly finished under extreme weft tension, and dried very thoroughly, to impart temporary set, which is lost as resorption of moisture takes place in storage. If such fabrics show excessive warp contraction after washing and relaxed drying, the defect is probably due to extension of the warp during finishing. If, on the other hand, the warp shrinkage is less than 2 per cent. the defect must be ascribed to incorrect cloth construction for the finished width in question.

Fabrics containing regenerated cellulose (see Shrinking, p. 900), rayons or fine filament cellulose acetate yarn which has been hydrolysed, are especially subject to dimensional instability.

Diminished Ease of Wetting

The time of wetting of a fabric frequently increases during storage, owing to coalescence of particles of fats, resulting in film formation, or to the oxidation of a wetting agent employed to improve an unsatisfactory finish.

Testing

Liability to evolve Amines. The principle of the test is to bring about migration of the amine by heating the fabric over acetic acid in a sealed tube and in close proximity to a sample of purified cuprammonium rayon fabric. Insoluble azo colours may contain difficultly volatile amines, but since such dyeings are usually resistant to bleeding, the test piece and the cuprammonium fabric may be superimposed and tested in contact without impairing the utility of the result. Specimens of aniline and diphenyl blacks, paramine

brown, and similar dyeings, are placed upon a stainless steel or similar grating in a jar, the bottom of which is covered with 10 per cent. acetic acid, the corresponding piece of desized cuprammonium fabric is similarly disposed, ¼ in. above the test piece, and the stoppered jar stored at 50° for a week. Frequently aniline blacks contain very large amounts of amine, and the acetic acid is deeply coloured in addition to the test piece.

Minute traces of amines, particularly aniline, can cause discoloration in acid atmospheres of all white textile materials within many yards of the source, and much serious damage has been caused by the presence of cloths containing aniline, especially in the holds of ships.

Treatment with nitrous acid, followed by thorough washing, removes all traces of amine, and it is rather surprising that so serious a defect should be tolerated.

When the presence of amines is suspected from the result of the acid storage test, it is advisable to test for paraphenylenediamine owing to the risk of dermatitis, which is always likely to be caused by this substance. The saffranine or indamine reactions may be used, but it is advisable to test for copper, which is sometimes present in sufficient quantity to decompose the hydrogen peroxide before the coloration appears.

Presence of Naphthols and Allied Bodies. The increased use for insoluble azo colours of passive components which are not readily removed, together with the replacement of cotton and linen by more absorbent fibres of regenerated cellulose, makes necessary the regular testing of dyed and printed goods coloured with these dyestuffs. The alkali salts of passive components are generally coloured, the alkali-free compounds are, with five or six exceptions, colourless, and the presence of these bodies may become evident only when the coloration is restored on washing in soap. Alternatively, exposure to light oxidizes the insoluble residues to resinous bodies of a brown colour. In addition, dermatitis may arise from the wearing of contaminated fabrics ; while normal people appear relatively resistant to the action of the β-hydroxynaphthoic and β-ketocarboxylic arylides, irritation undoubtedly arises, both when due to individual sensitiveness, and to the temporary depletion of the protective fats, which may cause the outbreak of skin troubles upon normally resistant people.

The most simple routine method of examination is to place upon the test piece a corresponding piece of desized cuprammonium rayon fabric, roll them together, bind with twine, boil for ten minutes in 1 per cent. oleate, and treat the cuprammonium fabric in a diazonium solution, when the passive components will couple to form a characteristic dyestuff.

Liability to Rancidity. Since exposure of a textile fabric to light involves exposure to air, which permits the volatile degradation products to escape as they are formed, stability to storage in warm atmospheres is a more important requirement.

As much of the fabric as can be inserted is kept in a stoppered jar at 50° for one or two weeks, and the odour observed when the stopper is removed.

Accelerated tests do not appear to correspond with the behaviour under less extreme conditions, but a low iodine value of the fatty matter is a reliable indication of satisfactory resistance to warm storage: hydrogenated fats are satisfactory after storage for several months in such conditions upon either protein or cellulosic fibres. In the experience of the writer, rancidity has arisen in the majority of cases, not from finishing agents, but from residues of lime and magnesium soaps, usually associated with traces of iron and copper.

Change in Shade of Dyestuff. This is a thorny matter, since a dyeing or print which does not change perceptibly after the first laundering is the exception rather than the rule, and in this respect present-day productions compare unfavourably with the corresponding productions of twenty years ago, although the ultimate fastness is greater.

Insufficiency of Conditioning. This is a frequent cause of colour variation, and cannot in all cases be distinguished from similar variations due to incomplete development of the shade after dyeing. Moreover, the oxidation or aggregation of the insufficiently developed dyeing may be completely inhibited if a permanent finishing process has subsequently been employed.

The writer suggests that colour variation due to lack of condition should disappear after air has freely circulated about the fabric for eight hours in the case of ordinary finishes, and twenty-four hours in the case of permanent finishes, light being excluded: variations which still persist are for commercial purposes permanent.

Acid-Sensitive Dyestuffs. Such dyestuffs are still employed, and a spurious resistance to acid atmospheres is imparted by finishing in alkali. Since the supply of alkali is limited, and the supply of acid is not, sensitiveness to acid constitutes a permanent defect.

Aniline black, in this as in other respects, requires individual testing, since it is usually acid-sensitive but finds universal application on economic grounds.

The test piece is suspended for half an hour in a jar, filled with SO_2, and having the bottom covered with water.

A good aniline black changes little; a commercial aniline black becomes greenish, but reverts to black after a day or two, while poor aniline blacks turn quite green, and are restored only by treatment

with oxidizing agents such as sodium dichromate. Diphenyl black should remain unchanged. Many dyestuffs are reduced by sulphurous acid and may form addition compounds with the sulphites present in wrapping paper; it is therefore desirable to apply the SO_2 test to all basic and soluble azoic dyestuffs.

Dyestuffs Sensitive to Nitrous Fumes. Dyestuffs containing primary and secondary amino-groups are diazotized and nitrosated by mixtures of NO and NO_2 in presence of mineral acid, and cellulose acetate dyestuffs, which usually contain these groups, are defective in resistance to storage in this respect; the matter has been investigated by Jones, Rowe and Chamberlain.

An accelerated test involves exposure in reproducible conditions to N_2O_3, which at normal temperatures is a mixture of NO and NO_2. The test specimen is padded in a 1 per cent. solution of sulphuric acid, dried gently, conditioned, and suspended in a jar connected with a gas jet, and fitted with a loop holding a small test-tube, which can be inverted by a second loop attached to the bottom.

For use, the jar bottom is covered with 85 per cent. nitric acid, and the test-tube charged with a standard weight of sodium nitrite. After the insertion of the specimen, the jar is swept with gas to remove air, and the gas stopped; the nitrite is discharged into the nitric acid and the necessary time (half to one hour) allowed.

These precautions are necessary owing to the instability of the NO; and the use of other acids or other concentrations of nitric acid alters the NO : NO_2 ratio as does the admission of air.

Insufficient Development. This is of two forms: the dyestuff may be in an unstable state of aggregation which is usually dichroic, or in an unstable chemical form; in either condition reversion to the more stable physical or chemical form is usually accompanied by a change of shade, which in most cases can readily be brought about by exposure to light. If sufficient time for a light exposure is not available the following methods may be employed.

Vat and insoluble azo dyestuffs in an unstable state of aggregation, and vat dyestuffs insufficiently oxidized, usually revert to the correct shade (on wool or silk) after soaping for ten minutes at 60° to 80° with a liquor containing 1 per cent. sodium oleate and 1 per cent. sodium perborate. Cellulose fibres should be boiled for ten minutes in water containing 1 per cent. sodium oleate, 1 per cent. sodium carbonate and 1 per cent. sodium *m*-benzenesulphonate, the latter serving as reduction buffer.

Indigosol dyestuffs, insufficiently hydrolysed and dyed on cellulosic materials, are usually oxidized by treatment in a solution containing 1 per cent. $CuSO_4$, 1 per cent. $FeCl_3$ and 1 per cent. H_2SO_4 at 70° for five minutes.

Indigosol dyestuffs upon animal fibres and cellulose acetate are sometimes developed with great difficulty. Treatment in 2 per cent. $NaClO_3$ with 5 per cent. H_2SO_4 at 70° for five minutes will usually produce the correct shade, but derivatives of indigo and indanthrone are injuriously affected.

All the above tests are liable to fail if the fabric has been subjected to permanent finishing operations; only the light exposure test is reliable.

The almost universal use of indanthrone or its derivatives for fast shades of blue necessitates a special mention of certain peculiarities. The presence of the dihydroazine group renders possible the occurrence of a more highly oxidized form which is greenish in shade and unstable. Many commercial dyeings are slightly over-oxidized, and show traces of the unstable form: this defect may be detected by rinsing the dyeing in 0·05 per cent. solution of $Na_2S_2O_4$, which restores the correct shade.

Insufficiently developed dyeings of indanthrone show a greenish tint due to the presence of highly dispersed amorphous dyestuff. This usually crystallizes to the correct shade during the soap test described above, but is much more stable if the fibre has been peptized in some finishing operation after dyeing.

Leuco-indanthrone is capable of condensation with formaldehyde, forming a greenish compound, chemically stable but less stable to light than indanthrone. This type of greening cannot be restored to the correct shade.

The indigosol form of indanthrone, which is particularly liable to incomplete chemical development, condenses in this condition with formaldehyde to form a chemically stable violet compound, which is not restored to the correct shade by the tests described above; incompletely developed dyeings show a similar violet shade which yields the correct shade when oxidized in presence of mineral acid.

In addition to the tests mentioned above, it is recommended that the tendency of vat, indigosol, and insoluble azo dyeings to stain a contiguous piece of white fabric when soaped in the absence of air should be tested as a matter of routine, since insufficiently developed dyeings of these colours may prove as defective in this respect as those produced from direct or acid dyestuffs.

Shrinkage. Measured test pieces of the fabric are placed upon a stainless steel wire tray without tension, and conditioned for twenty-four hours at 100 per cent. R.H., and the shrinkage noted. Weft shrinkage is more serious than warp shrinkage, since the former may render the cloth unserviceable, whilst the latter is not usually important unless very marked (more than 2 per cent.). Unshrinkable finishes should show no change whatsoever in this test.

Loss of Tensile Strength. So many possible causes of degradation during storage exist that no single test is satisfactory.

Acids capable of hydrolysing cellulose present in the fabric are readily detected by ironing sample pieces, portions of which have been washed thoroughly in 1 per cent. borax, rinsed, and dried for a definite period with a thermostatically controlled iron.

The liability to develop acid, which may be formed from sulphur dyestuffs, or the presence of organic esters of nitric, phosphoric, oxalic or tartaric acids, will be indicated by the weathering test or storage at high temperatures (see Wear, p. 929), but if the fabric shows an alkaline reaction, or the presence of buffer salts, such as sodium acetate or borax, when titrated with mineral acid, it is advisable to extract half of the test pieces with distilled water, to elucidate the extent of the possible change. The same will apply to deterioration from oxidation, or hydrolysis by neutral salts.

Presence of Oxidation Catalysts. The rancidity of fats, the oxidation of sulphur, and of unsaturated hydrocarbons, such as rubber, is much accelerated by the presence of iron, copper, and manganese. These metals are frequently present in sulphur dyestuffs and sometimes in direct dyestuffs to such an extent that the fabric readily causes hydrogen peroxide to effervesce when warmed; furthermore, it is common practice to treat dyeings of insoluble azo-colours, direct colours, and sulphur colours with copper in order to improve resistance to light. It is a useful check upon the storage test to examine for traces of the metals mentioned by warming with hydrogen peroxide (10 per cent.), and confirming by specific qualitative tests.

If fabrics are to be coated with any form of rubber this precaution should always be taken.

It must be remembered in this connection that metals present as complex anions, oxalates, tartrates, double fluorides, etc., are much less active than as cations; the catalytic activity is not therefore proportional to the quantity of metal present.

R. RESISTANCE TO WEAR

No well-known process of finishing has as its principal object the increased resistance of the fabric to "wear," by which we generally mean frictional wear, but some finishing processes have this effect in some degree, for instance, finishes which include stiffening or glazing, particularly if the finish is "permanent" or not affected by washing. Often, however, resistance to wear is reduced by some of the finishing processes owing to degradation caused generally by some defect in processing. Conditions which promote oxidation, the presence of acid, excessive heating, and excessive pressure in calendering,

beetling and schreinering are common sources of trouble. Fabrics showing abnormally low resistance to wear generally exhibit also a diminished strength and resistance to ripping. Such fabrics are often classed as "degraded" whether the degradation is due to chemical or to physical causes. There appears some support for the claim that wear tests are a better criterion of degradation than tensile tests, since degradation often seriously reduces the elastic character of a fabric without greatly affecting the tensile strength. Such degraded fabrics are sometimes said to be "brittle," and this lack of elasticity suggests that wear tests, ripping tests and "ballistic" tests (work done in rupture) will often be more useful and easy of interpretation than tensile tests. For this and for other reasons it is wise to regard wear tests as being as yet very imperfectly understood, particularly if they are to be considered as an indication of the life of garments subjected to frictional wear.

When the fabric is employed for special purposes, for example, typewriter ribbon or lamp shades, which involve endurance in certain definite conditions, the question is relatively simple, and the useful life can be determined with accuracy by testing in the typewriter, or in the light of the carbon arc.

It should be remembered that an article may be discarded as "worn-out" for a number of reasons. At the one extreme the intrinsic strength of the material may be quite unimpaired, but it may be soiled or the original finish may be spoiled and there may be no simple method of cleaning it and restoring the finish. Often defects in appearance such as local fading, wearing-off of "nap" and presence of shine are the deciding factors. On the other hand, an article may be worn until it ruptures when very small stresses are applied. In use the loss of resistance, however caused, is mostly made evident by a tear or a burst—often while the material is being laundered. It would seem sounder therefore to subject material to be tested to the degrading influence under standard conditions of intensity and duration, and then to determine the loss of resistance, either by breaking tests or by bursting tests.

Many attempts have been made to measure resistance to wear in this way by submitting all the specimens to a standardized amount of wear and then taking tensile tests or estimating the loss in weight, but significant and useful results have not yet been obtained.

In tests adapted to predict the resistance of a material to attrition, the rubbing is effected either by a cutting abrasive or by some softer material. In the first case the structure of the material under test will be weakened by abrupt local shearing of the constituent fibres, in the latter the fibres will be broken by repeated plucking stresses, so that, in general, the compactness of the thread and the hardness of the

fibre will be determining factors for the one kind of wear, and the elasticity and looseness of twist will control the other.

Wear-testing machines for fabrics increase in number every year, and it is not intended to do more than offer a very general comparison as to their capabilities. The earlier machines employed sandstone, emery, and steel cutters or wires as abrasive surface, but more recently, and perhaps because garments are not often worn out by contact with such material, the tendency has been to use softer material, such as bristles of horse hair or fabric made from cotton or wool.

Many, perhaps most, of the machines involve reciprocating movement between the abrasive and the test specimen, while in others the movement is rotary. Reciprocating machines must be used, of course, where it is desired to distinguish between the resistance to wear in warp and weft, or according to the direction of twill surface, but it is claimed for rotary machines that garments are commonly subjected to wear in all directions and that the fabric is worn out as soon as one set of threads has been worn out or broken. Rapidity of testing and simplicity of structure is claimed for the rotary machine.

It is always difficult to standardize the end-point of a wear test, that is to say, the number of revolutions of the machine, or the time, which indicates that the specimen is to be regarded as being worn out. Sometimes the fabric is regarded as worn out when a loaded strip is completely broken by wear and by the tension imposed upon it during the test, but such a test to complete destruction can be of very little value when one set of threads, warp or weft, is completely worn out before the other.

Since a fabric is generally worn out, or at least seriously worn, when any of the threads are worn through, it is common to regard the end-point as that when a certain number of threads, generally one or two, are found on careful examination to be severed. Such careful examination is often tedious and liable to lead to discrepancy between the results of different operators, but this end-point appears to be more defensible than any other yet proposed.

The useful life of a fabric corresponds to that amount of friction to which a garment has been exposed on the person and in laundering, and which renders the garment no longer serviceable. A fabric may be regarded as worn out when one or more threads are worn through or severed by friction, and the same " end-point " may be considered to apply to specimens of fabric worn out in any testing machine. The definition is, of course, arbitrary, but it provides a simple and direct figure of merit applicable to a very wide range of fabrics. This simplicity of interpretation does not seem to extend to tests requiring a certain amount of wear upon a sample, followed by determination of loss of weight, or of loss in strength.

In the very imperfect state of our knowledge of the value of wear tests, and as no one has yet attempted to compare the results obtained with many of the existing wear-testing machines and methods, or even with the best known of them, the writer can do no more than state his own experience. He has for some years had the task of dealing with a large number of complaints of wear, among other complaints received from the users of articles of cotton and rayon wearing apparel made from a considerable number of different fabrics and has had the opportunity of making wear tests upon them all. It has not been difficult from the result of a wear test to place these fabrics in ascending order of merit, and to place the equivalent garments in order according to the number of complaints of poor-wearing properties recorded against each. Correction had to be made for the fact that the fabrics are sold in varying known quantity. While many disturbing factors exist and the correlation is not perfect, it can be said that the order of merit given by the tests corresponds fairly well with the frequency of the complaints. While the primary object of the tests was to avoid the sale of fabrics which could not be expected to give good service to the wearers of the garments, these trials have also given considerable confidence in the methods of testing employed.

Another writer who has had wide experience in the testing of shirtings and other fabrics of wearing apparel, and who has used several kinds of wear-testing machines. some of which he has himself devised, arrived at the following conclusions :—

(1) While convinced that the method of using a fabric as its own abrasive (the " cloth on cloth " test), should be significant as a means of forecasting the comparative life of different fabrics, he has failed to find any support for that theory in his own experience.

(2) He condemns methods whereby samples are submitted to a certain amount of wear in testing, followed by a test of loss in weight or of tensile strength, because he cannot attach any single " figure of merit " to the results and has failed to find the results to be significant.

(3) While he condemns methods which employ carborundum-like abrasives, he finds reasonable agreement and significance of results whether a standard wool or cotton cloth is used as abrasive, or whether steel wires (card clothing) are trailed over the fabric under test.

(4) His favourite test for regular and rapid routine testing purposes may be shortly described as follows : A small piece of the fabric to be tested is stretched over a ring about 1 in. in diameter and mounted upon a spindle so that the ring may be revolved in its own plane. A similar ring is covered with a similar small piece of " standard " wool fabric to be used as abrasive. The faces of the two fabrics are then brought into contact under a " standard " load, so that they are parallel to each other, but with the axes of the supporting spindles displaced

by about half an inch. Both spindles are then revolved, the revolutions being counted, until the fabric under test is " worn out," the end-point being recorded when any two threads are found to be severed. A partially worn-out ring of fabric is thus produced, and it is easy to see whether the warp or the weft gives way first.

(5) It is claimed that the above method yields results which will place a number of different fabrics in about the same order of merit as is shown by the behaviour of those fabrics in use as garments. Though the evidence is by no means complete, it is generally found that fabrics which give low results under this test give rise to complaints from the wearers of garments, but that higher test results are seldom or never accompanied by complaints.

In the experience of a third writer, abnormal rapidity of attrition arises from friction between two layers of the same fabric, as must occur frequently with shirting materials, and examination of worn-out garments indicates that rubbing during laundering, especially of the cuffs and front, has taken place, and that the resistance to this type of attrition usually determines the life of the garment. The result is to be expected, since the projections upon the surface of one piece of cloth will tend to fall most readily into the depressions on the surface of a second piece of cloth when this possesses warp and weft yarns identically spaced and of the same count and twist. More perfect interlocking of the surfaces will occur therefore when the cloths are pressed together, and greater damage will be done when they are moved laterally. It may seem, therefore, that this type of abrasion will give more logical results than when surfaces made up by cutting units, such as emery or card clothing, are employed.

The tests dealt with above are generally tests of resistance to wear of the surface of a fabric, taking no account of the friction of the fibres upon each other beneath the surface of the fabric. Internal attrition may be of importance when the warp and weft are of dissimilar fibres ; the harder fibre abrades the softer, especially in the wet state, and since the conditions are such as arise in a rotary washing machine fabrics containing dissimilar yarns, usually cotton warp and rayon or silk weft, should be subjected to an attrition test in the wet state.

Some tests have been devised in an endeavour to imitate conditions of wear in which flexure of the fabric is combined with surface friction. Such a test consists in bending a strip of fabric under tension over a carborundum rod, giving it a reciprocating movement, and proceeding with the movement until an arbitrary end-point is reached. In another test of similar character, the rolling-crease test, a folded edge of the fabric is made to roll between roughened metal surfaces pressed against the fabric.

General Conditions of Testing

The resistance of fabrics such as shirting, dress fabrics and overalls to wear, as shown by any testing machines, would appear to be best indicated by carrying on the "imitative" wear until the fabric is in such condition that it may reasonably be regarded as worn out and no longer serviceable. But while this generality is commonly accepted, widely different opinions exist regarding :—

(1) The abrasive to be employed.
(2) Direction of the applied friction, whether separately in warp and weft directions with reciprocating motion, or in all directions.
(3) The means of obtaining a satisfactory end-point.

As in all wear tests, the value of the result depends finally upon whether reasonable agreement is found between that test result and experience regarding the useful life of garments made from the same fabric.

The moisture content of fabrics submitted to wear tests is of the greatest importance ; and it is important to know whether they have been shrunk or stretched, whether they contain lubricants, fillers or other finishing substances. For most purposes it is desirable to have fabrics thoroughly scoured, shrunk and "conditioned" before submission to the test, in order that reasonable comparison may be made. The conditioning generally consists in exposure to an atmosphere of 75 per cent. R.H. until the weight remains constant.

In this, as in other types of testing, much more information may often be obtained when it is possible to obtain control samples at another stage of fabrication. In certain investigations this is necessary ; for example, if the influence of a finishing treatment upon the wearability of an article is to be determined, samples of the untreated fabric should be used for comparison, since the finished fabric can seldom be restored to its original condition.

Widely varying results are commonly obtained as between separate specimens taken from the same sample of fabric, depending largely upon the degree of uniformity in the yarn and fabric structure. Reliable results are seldom obtained by taking the average of five tests, but twenty tests are generally found satisfactory. Wear tests have sometimes been condemned by reason of this difficulty in obtaining uniformity, but the variation is comparable with other recognized tests such as the ripping test.

Testing Machines

It will be seen that considerable divergence must exist between the interpretation placed by different workers upon the results of wear tests. In addition the type of testing procedure appropriate for one class of material may be quite unsuitable for another. This leads to the design of special machines with a restricted scope. It is, however, important that the conditions under which a particular class of test is made should be standardized throughout the industry, since the results obtained by one worker are then intelligible to others. Until experience of the peculiar conditions which affect the results of wear tests in a particular works have been obtained, it is better to obtain a machine designed by a maker of some repute or to the design of some experienced authority. With the object of showing the kind of machine that is easily available, two or three representative types will be discussed, and something will be said about the methods of operation.

The earliest forms of machine depended upon subjecting the surface of the cloth to a rubbing or scraping action with knives or metallic projections ranging from sharp to completely blunt and rounded edges. The scraping elements were either mounted on a roller—after the manner of a shearing machine—and engaged with the surface of the cloth held stationary under a predetermined tension, or the rubbing element remained stationary and the cloth sample was reciprocated.

Hassler's Machine.[1] Hassler's machine was held by Kertess to be incorrect in design since the blades on the roller gave a beating as well as a rubbing effect and the result depended upon the stretch and other irrelevant qualities of the cloth. A pure scraping action was attained either by using rollers with sharply engraved riffles or special carborundum rollers. Carborundum has the advantage that the cutting points are not easily blunted owing to the hardness of the material. Kertess, after many attempts to get the surfaces of different materials in a comparable condition, made the unusual suggestion that this should be done by chemical means as follows: The pattern is treated for forty-five minutes at 94° in 40 times its weight of 0·084 per cent. hydrochloric acid, rinsed well in distilled water, squeezed, extracted thoroughly with ethyl alcohol, dried at 65° to 70° and conditioned in a drying cupboard at 25° until required for testing.

Muller Machine.[2] In this machine the two surfaces of the same cloth are rubbed one against the other. The two surfaces are formed

[1] Hassler A.G., Berne; see v. Kapff, *Farber-Zeit.*, 1908; v. Kapff and Repenning, *Mell. Textilber.*, 1923, 181.
[2] Made by H. Keyl of Dresden, cf. *Textil-Forschung*, 1922, 95; *Leipsig Monatschr. Textilind.*, 1926, 38.

by clamping a single layer of the cloth upon a shoe. The under shoe is stationary while the upper shoe moves backward and forwards in a straight line. A loading arrangement, operating upon the upper shoe, brings the two pieces of cloth together with a definite pressure. Instead of rubbing two similar pieces of cloth together, one of them may be replaced by felt, leather, emery paper or other abrasive substance. The following directions will help to obtain reliable and consistent determinations. This tester is most conveniently used with a single layer of the fabric stretched upon each shoe; the working surfaces of the shoes should be perfectly plane, and should be faced with burnished stainless steel or chromium plate. The test pieces should be set perfectly square upon the shoes, and a standard tension should be used for each loading of the upper shoe: a simple and convenient means of ensuring this is by clamping one end of the test piece, and applying the tension by means of a strong paper clip, attached to a small spring balance, prior to fixing the second clamp. Test pieces should be freed from unfixed lubricant by washing as described above. The load upon the upper shoe, number of rubs, and rate of rubbing are standardized, and the strength of the abraded strip is then determined. The wearing properties of the material should be determined when the rubbing is applied in the direction of the warp and also, separately, when applied in the direction of the weft.

Very strong fabrics, such as collar cloths, usually fail in wear owing to very rapid abrasion at creases, for example, along the folds of collars and shirts. In the selection of fabrics which must show endurance in such conditions, the rate of abrasion of the plane surface has no direct relation to the endurance of the cloth when rubbed at the fold.

In such cases a pack of twenty or thirty test pieces suitable for the tensile or ripping test must be prepared: shirting materials are usually creased along the warp, dress fabrics diagonally along the bias, and the test pieces should be cut accordingly; the test pieces are folded accurately along the line to be tested, ironed individually, and fixed in a small clamp, the folds forming the wearing surface of the upper shoe, to which the clamp is secured. This is reciprocated with the folds at right angles to the direction of motion, so allowing any slight uneven projections above the mean surface of the assembly to adjust themselves. This will not take place if the folds are parallel to the line of travel.

Resistance to folding may be measured by a machine built by Schopper of Leipzig. A thin strip of cloth is stretched between two spring-tensioned jaws. In the centre of the strip is a grip which is oscillated at right angles to the plane of the cloth, flexing it until it breaks. The number of strokes is counted on a suitable counting

mechanism. When the cloth breaks a knock-off motion stops the machine.

Machine of the Linen Research Association.[1] This machine (Fig. 147, p. 928) also uses a reciprocating motion between the cloth surface and some abrasive surface. The material is prepared as a strip 2 in. wide by pulling down a wider strip in a manner similar to that used in testing the tensile strength of cloth. On heavy fabrics a narrower strip is used. The strip of cloth is held with its length in a vertical direction. The upper end is clamped in a movable jaw, the lower end in a jaw which is weighted with a tension. Different tension weights can be used, corresponding to the type of cloth under examination. The lower jaw is held in guide rails, so that it can move only up and down and cannot turn. Engaging with the central area of the suspended strip is a flat shoe which is covered with the rubbing material. Usually this is of a standard grade carborundum, but other materials, including the cloth itself, can be substituted. The shoe is pressed against the strip with a predetermined pressure (this may be adjusted). The upper jaw is oscillated transversely to the length of the strip (*i.e.* horizontally) with a stroke 4 in. in length repeated 100 times per minute. The strip is thus given a radial movement which results in abrasion taking place in a direction at right angles to its length, while at each stroke the warp and weft threads are displaced slightly, relative to each other, and imitating to some extent the stresses to which the cloth would be subjected in wear. It is also claimed that this type of movement breaks down any binding effect exerted by finishing treatments upon the fibres of the yarns.

Although this machine may be arranged to give a fixed number of rubs, after which the specimen may be removed and examined, it is normally operated so that rubbing is continued until the cloth is worn through completely. Finally, under the weighting load, it breaks, and the shoe, no longer held back by the cloth, swings forward on its suspension, and in so doing operates a mechanism which stops the oscillation counter. Three separate testing units, allowing three strips to be put under test at once, are built into one machine. When all three strips are broken, the machine stops.

A number of machines depend upon some kind of rotary motion between the cloth and the abrading surface. Belonging to this class is the—

Herzog-Geiger Tester.[2] The cloth is stretched over a hard hemispherical shoe. This is given a simultaneous rotary and rocking movement. Pressing against the cloth with a predetermined pressure is a flat surface covered with emery paper. The motion of the machine

[1] Goodbrand & Co. Ltd., Stalybridge and Manchester.
[2] L. Schopper, Leipzig.

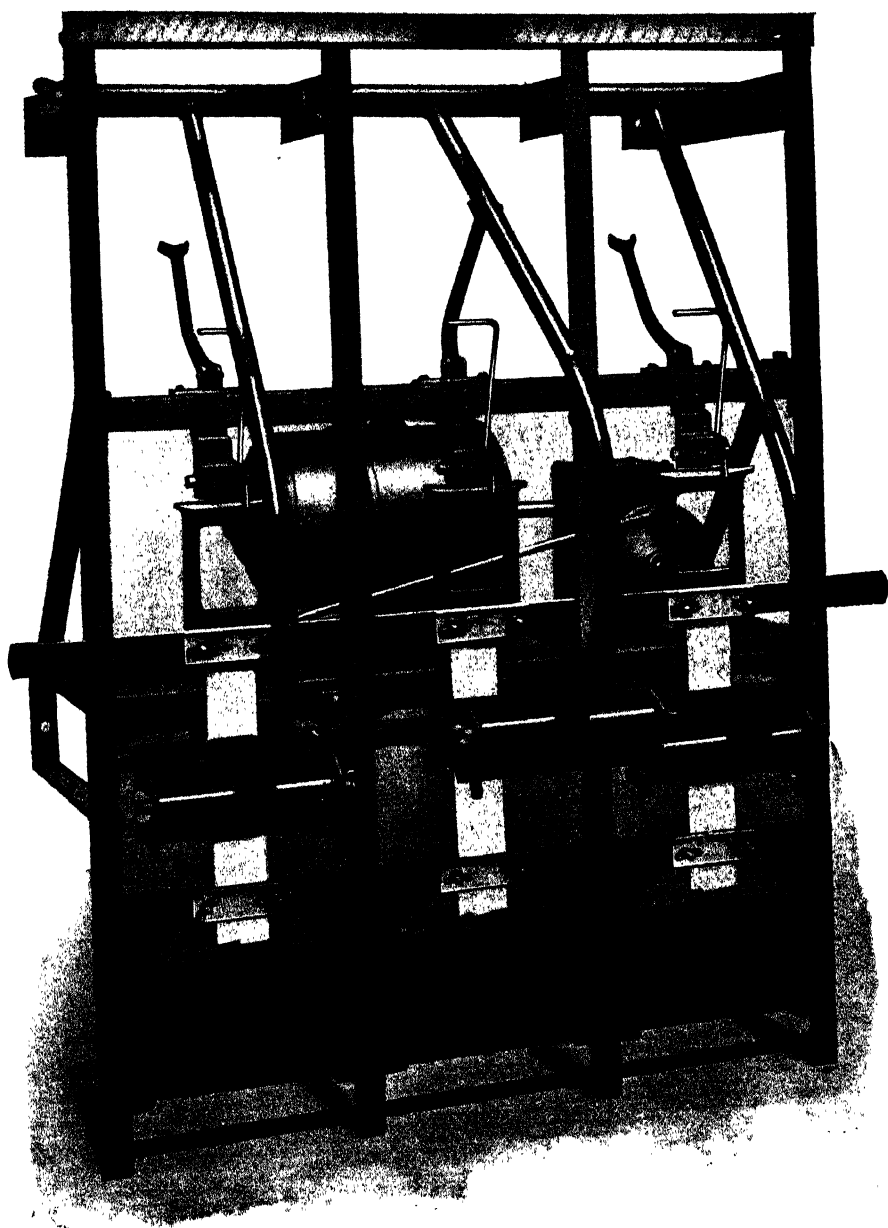



Fig. 147.—Cloth-wear Testing Machine.

is intermittent, giving the displaced fibres opportunity to settle before further rubbing takes place.

A very simple machine which has been designed and used extensively by a large textile firm is the

Ring-Wear Tester.[1] In this machine a small square of the cloth to be examined is stretched, by means of a rubber band, face upwards over a small, horizontal, ring-shaped shoe. A standard woollen cloth forming the abrasive is stretched face downwards upon a similar shoe. Each ring is rotated at the same speed, and the two cloth surfaces are brought together under a fixed pressure. Rubbing results because the axis of rotation of one shoe is not in the same straight line as the axis of the other. Both axes are kept vertical, but are a short distance (roughly equal to the radius of one of the shoes) apart. The revolutions of the rings are measured by a suitable counter.

Chemical Degradation.—In wear, fabrics are degraded by the action of light, oxidizing agents, acids and high temperatures, all in the presence of evaporating water, the whole process being conveniently summarized by the term "weathering." Any practicable test of endurance must therefore combine these influences in proportions as nearly correct as possible, but of a greater intensity than encountered during normal use. The influence of acid and alkali must, of course, be determined separately.

The method suggested consists essentially in determining the time of exposure to light from the enclosed carbon arc necessary to reduce the tensile strength of the fabric by a given proportion, or else to a figure which represents the minimum useful strength. A somewhat high temperature of testing may need to be established since curtains behind glass have attained more than 75° in stagnant air, when exposed to summer sunshine in Europe.

The equipment required comprises a Fadeometer, provided with an annular water-bath, the cover of which is cut away to allow insertion of samples surrounding the interior of the cabinet. The bath should be of rhodium plate on silver-plated nickel sheet, fitted with an adjustable thermostat, and constant level control; in testing, strips of the fabric are cut to size suitable for the tensile test, and suspended half above, half below, the water level, loosely fastened at top and bottom by means of pure bleached cotton thread to a silica framework; the bath is filled either with a solution of 0·01 per cent. Na_2CO_3, or one containing 0·02 per cent. $NaHSO_3$ and 0·01 per cent. NaCl in distilled water (depending upon whether acid or alkaline conditions require to be established) until the water-line is exposed to the arc. The solution should be maintained at 75°. Strips should be removed every two and a half, five or ten hours,

[1] Baskerville and Lindsay, Manchester.

according as the fabric is light, medium or heavy in weight; thick canvases and blind fabrics may require exposure alternately upon each side, since the radiation and evaporation act superficially. A series of ten strips will usually be necessary for each test.

The necessity for purifying the test pieces prior to exposure must be decided in each case by the judgment of the tester, since casements and furnishing fabrics appear to be washed very infrequently, whilst shirtings and handkerchiefs are frequently washed by the manufacturer prior to sale. Usually it is safer to purify two or three strips by soaping, and to leave these for the longest exposures, together with corresponding untreated strips.

The exposed strips should be washed in soap and soda to remove the water-line deposits, prior to the tensile test. The test as described above is dependent upon the rate of evaporation from the surface of the test pieces; as this is very difficult to control, samples of standard material should be placed at intervals round the cabinet.

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Atomic No.		Symbol.	Atomic Weight.	Atomic No.		Symbol.	Atomic Weight.
13	Aluminium	Al	26·97	60	Neodymium	Nd	144·27
51	Antimony	Sb	121·76	10	Neon	Ne	20·183
18	Argon	A	39·944	28	Nickel	Ni	58·69
33	Arsenic	As	74·91	41	Niobium Nb (=Columbium Cb)		92·91
56	Barium	Ba	137·36	7	Nitrogen	N	14·008
4	Beryllium Be (=Glucinum Gl)		9·02	76	Osmium	Os	190·2
83	Bismuth	Bi	209·00	8	Oxygen	O	16·0000
5	Boron	B	10·82	46	Palladium	Pd	106·7
35	Bromine	Br	79·916	15	Phosphorus	P	31·02
48	Cadmium	Cd	112·41	78	Platinum	Pt	195·23
55	Caesium	Cs	132·91	19	Potassium	K	39·096
20	Calcium	Ca	40·08	59	Praseodymium	Pr	140·92
6	Carbon	C	12·010	91	Protoactinium	Pa	231
58	Cerium	Ce	140·13	88	Radium	Ra	226·05
17	Chlorine	Cl	35·457	86	Radon	Rn	222
24	Chromium	Cr	52·01	75	Rhenium	Re	186·31
27	Cobalt	Co	58·94	45	Rhodium	Rh	102·91
29	Copper	Cu	63·57	37	Rubidium	Rb	85·48
66	Dysprosium	Dy	162·46	44	Ruthenium	Ru	101·7
68	Erbium	Er	167·2	62	Samarium	Sa	150·43
63	Europium	Eu	152·0	21	Scandium	Sc	45·10
9	Fluorine	F	19·00	34	Selenium	Se	78·96
64	Gadolinium	Gd	156·9	14	Silicon	Si	28·06
31	Gallium	Ga	69·72	47	Silver	Ag	107·880
32	Germanium	Ge	72·60	11	Sodium	Na	22·997
79	Gold	Au	197·2	38	Strontium	Sr	87·63
72	Hafnium	Hf	178·6	16	Sulphur	S	32·06
2	Helium	He	4·003	73	Tantalum	Ta	180·88
67	Holmium	Ho	163·5	52	Tellurium	Te	127·61
1	Hydrogen	H	1·0078	65	Terbium	Tb	159·2
49	Indium	In	114·76	81	Thallium	Tl	204·39
53	Iodine	I	126·92	90	Thorium	Th	232·12
77	Iridium	Ir	193·1	69	Thulium	Tm	169·4
26	Iron	Fe	55·84	50	Tin	Sn	118·70
36	Krypton	Kr	83·7	22	Titanium	Ti	47·90
57	Lanthanum	La	138·92	74	Tungsten	W	183·92
82	Lead	Pb	207·21	92	Uranium	U	238·07
3	Lithium	Li	6·940	23	Vanadium	V	50·95
71	Lutecium	Lu	175·0	54	Xenon	Xe	131·3
12	Magnesium	Mg	24·32	70	Ytterbium	Yb	173·04
25	Manganese	Mn	54·93	39	Yttrium	Y	88·92
80	Mercury	Hg	200·61	30	Zinc	Zn	65·38
42	Molybdenum	Mo	95·95	40	Zirconium	Zr	91·22

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